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Performance Specification Tests for Pollutant and Diluent Gas Monitors Reporting Requirements, Report Format, and Review Procedures

Entropy Environmentalists, Inc.
Research Triangle Park, NC

Prepared for

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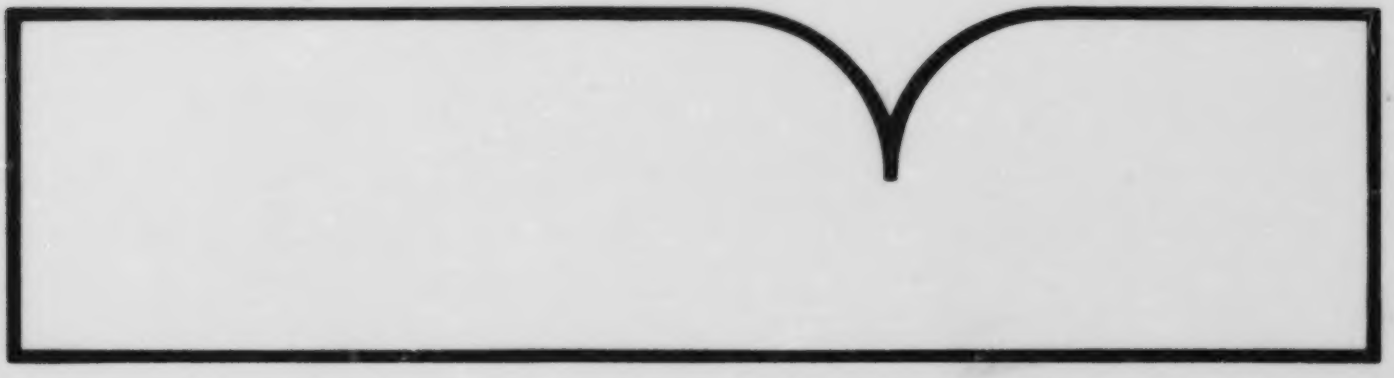

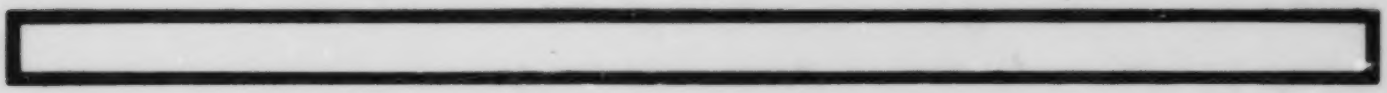

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1.0 INTRODUCTION

Continuous monitoring of gaseous pollutant emissions -- sulfur dioxide (SO_2) and nitrogen oxides (NO_x) -- is required at stationary sources subject to New Source Performance Standards (NSPS). Requirements for continuous monitoring are contained in 40 CFR 60.13. Paragraph 60.13(c) states that "the owner or operator of any affected facility shall conduct continuous monitoring system performance evaluations and furnish the Administrator within 60 days thereof...copies of a written report of the results of such tests." The contents of this written report are mentioned in Performance Specification 2 (40 CFR 60, Appendix B), which explicitly requires reporting of the following information:

(1) The data and results from determinations of:

(a) Calibration gas concentrations (Figure 2-1).

(b) Calibration error (Figure 2-2).

(c) Relative accuracy (Figure 2-3).

(d) 2-hour zero and calibration drifts (Figure 2-4).

(e) 24-hour zero and calibration drifts (Figure 2-5).

(f) Response time (Figures 2-6).

(2) The method used to determine the integrated averages from the continuous emission monitor for the relative accuracy test (this requirement appears as a note at the bottom of Figure 2-3).

(3) For relative accuracy tests of wet-basis continuous emission monitors, the moisture test method and the correction procedure employed to place the reference method and monitoring measurements on a consistent basis.

Moreover, additional reporting may be necessary depending on the manner in which the Reference Methods are employed during the performance testing program (which may commence with the analyses of calibration gases two weeks prior to the initiation of the operational test period). Thus, the introduction to 40 CFR 60, "Appendix A - Reference Methods" addresses the necessary reporting requirements to be observed when the tester elects to employ materials or procedures identified therein as "optional," "equivalent," or "subject to the approval of the Administrator."

A performance test report containing only the explicitly required information would provide little support for the results of monitor performance testing. Indeed, this type of support is critical to prove that the monitors, as operated and installed at the source, are providing quality emission rate data because subsequent decisions and actions presuppose the accuracy of the indicator, i.e., the continuous monitor.

This manual has been written with a threefold purpose:

(1) Provide a model for the complete reporting of the results of continuous monitor performance tests.

(2) Provide test report reviewers with sufficient background information about the continuous monitor performance specifications so that they may review such reports effectively.

(3) Provide test report reviewers with detailed guidelines for conducting reviews so that the review process may be facilitated.

The interpretation of "reporting completeness" is not entirely objective, and the recommended reporting requirements contained in this manual may be viewed by some as burdensome. However, the recommendation includes only the reporting of data generated as a matter of course, if the procedures detailed in the Performance Specifications and Reference Methods are followed. In

addition, the material based on report formatting and stylistic conventions (e.g., Introduction, Table of Contents, Discussion of Results, etc.), would also be included as a matter of course in engineering report documentation.

Standard, complete performance specification test reporting can have beneficial effects. It will promote adherence to Performance Specification and Reference Method procedures, which in turn will help ensure quality services to sources who contract for testing. For the agency, standardized, complete reporting can facilitate consistent comparisons of performance among many monitors (which may be useful in recognizing invalid emission rate data), ease manpower restraints, and increase the cost effectiveness of continuous monitor certification programs.

This manual is intended to accompany the continuous monitor Performance Specifications promulgated October 6, 1975 (Federal Register, Vol. 40, No. 194, pp. 46250-46271). Since that time, however, revisions to these Performance Specifications have been proposed twice: Federal Register, Vol. 44, No. 197, Wednesday, October 10, 1979, pp. 58601-58636, and Federal Register, Vol. 46, No. 16, Monday, January 26, 1981, pp. 8351-8363. The revisions proposed October 10, 1979 were quite extensive in scope, and in addition, the revisions addressed required reporting in some detail. The revisions proposed January 26, 1981, on the other hand, are significantly streamlined relative to the currently promulgated Performance Specifications, and emphasize the assessment of performance in terms of the relative accuracy test results. Both revisions require determinations of system relative accuracy in terms of lb pollutant/10^6 Btu when diluent monitors are used in conjunction with pollutant monitors. Thus, the revisions implicity include a relative accuracy specification for diluent monitors. Revised Performance Specifications in the form of those proposed January 26, 1981, are favored for promulgation.

Other regulatory actions and issues that may ultimately affect the use of this manual include: (1) the introduction of additional Reference Methods for determinations of SO_2 and NO_x emission rates (lb pollutant/10^6 Btu); (2) revisions to the current Reference Methods so that quality assurance provisions are included; and (3) the promulgation of Appendix F, which will specify quality assurance programs for continuous monitors.

In spite of the current regulatory flux, it is hoped that this manual will establish uniform reporting requirements and be a useful guide for reviewers of performance test reports.

Although this manual explicitly addresses monitor performance test report requirements for NSPS sources, much of this information may apply to reports for monitors installed at sources subject to State Implementation Plans (SIPs), since many of the continuous monitoring requirements contained in the SIPs are patterned after the specifications and procedures of 40 CFR 60, Appendices A and B. For similar reasons, applicability may extend to continuous monitors installed as required by waivers, consent decrees, etc.

This manual is divided into five sections. Section 2.0 provides background material concerning the nature of the report and also discusses the review process. Included within the background material are discussions that deal with: (1) the function of the pretest meeting, any ensuing test protocol decisions, and the use of this information by the reviewer; and (2) the role of the agency observer during the test and the use of the observer's report and field notes by the reviewer.

Following this information, the goals of the review are listed. These goals are the basis for subsequent discussions that address (a) procedures for reducing the complexity of the reviewing task; (b) the organization and strategy of the review; (c) the depth of the review; and finally, (d) the actions the reviewer should take upon completing the review.

Sections 3.0 and 4.0 deal with the reporting format and requirements and the review of pollutant gas monitor performance test reports. The material is divided into the two sections for convenience. Section 3.0 is covers the body of the test report: the introductory background information; the source, monitor, and test descriptions; and the test results. The discussions focus on the format, content, and purpose of this introductory material.

Section 4.0 deals with the raw data generated during performance tests of gas monitors. Each test of the complete performance specification test is separately introduced and discussed. Each introduction includes a brief description of the test and its purpose. The discussions that follow address reporting format, reporting requirements, and review procedures. Additional data that supplement the tests, such as data generated by moisture determinations, are also included in Section 4.0 and are treated similarly.

Section 5.0 addresses the reporting and review of the raw data accompanying performance test reports of diluent monitors. Because the performance tests of diluent monitors closely parallel those of gas monitors, much of Section 5.0 is devoted to directing the reviewer to analogous discussions pertinent to gas monitors (the subject of Section 4.0).

2.0 DISCUSSION OF THE REVIEW PROCESS

This manual is designed for the novice reviewer. The reviewer is expected to have some familiarity with Methods 3, 4, 6, and 7 (40 CFR 60, Appendix A) and Performance Specifications 2 and 3 (40 CFR 60, Appendix B). As the reviewer gains experience, this manual should become more a reference, rather than a guide. This is especially true of the many introductions to the individual test procedures.

2.1 AN OVERVIEW

The primary goal of the test report review is to determine the performance status of the tested monitor.

Clearly, the amount of data and supporting information contained in the report will limit the accuracy of the continuous monitor performance assessment. Sufficient data should be reported to allow *a priori* recalculation of the test results from the field data, laboratory data, and monitor records. Accordingly, completeness is the primary aspect of the report to be assessed by the reviewer.

The reviewer must determine whether acceptable testing procedures were employed in the monitor performance evaluation. In general, test procedures must provide accurate data for determining whether the monitor is in compliance with the performance specifications. Finally, the reviewer must determine whether the reported test results have been calculated correctly and accurately from the reported data.

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Based upon the results of the report review, the reviewer must conclude that:

(1) the reported results of the test conform with the applicable monitoring specifications,

(2) the reported results do not conform with the monitoring performance specifications, or

(3) the performance status of the continuous monitor cannot be determined from the reported results.

A complete monitor test report includes a plethora of information. Figure 2.1 illustrates the complexity of the complete review process for an SO_2 monitor relative accuracy test. The diagram also shows how the review can be effectively approached by employing two guidelines: (1) divide the review into workable units, and (2) work from general to specific (e.g., first check the final result; second, the supporting intermediate results; and, finally, the raw data).

2.2 PREPARING FOR THE REVIEW

Before starting the review of a monitor test report, the reviewer should assemble as much supplementary information as possible. This may include the following:

(1) pretest protocol statements;

(2) observer's report, notes, or checklist;

(3) previous monitor performance test reports; and reports; and

(4) previous source performance test reports.

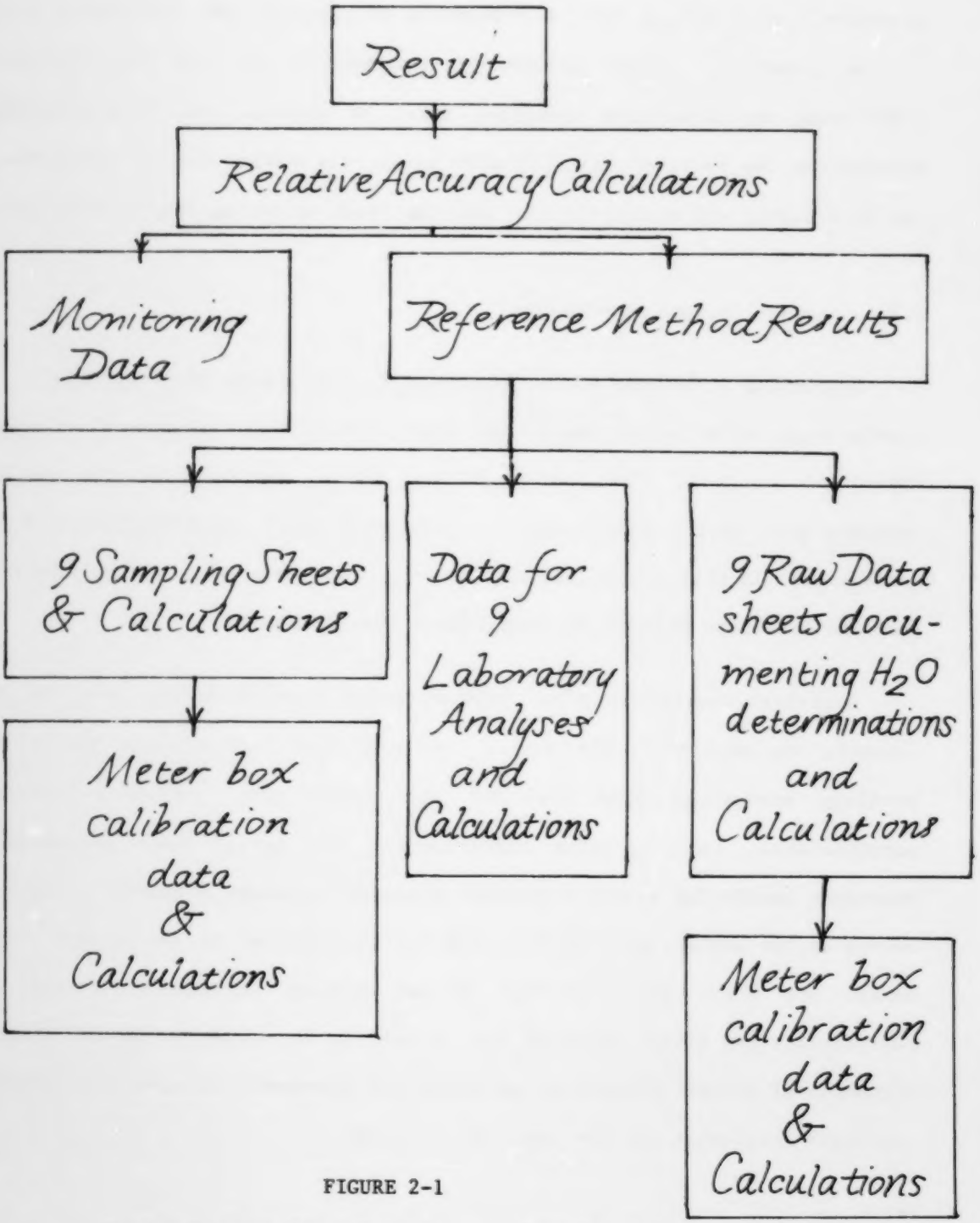
Result
Relative Accuracy Calculations
Monitoring Data
Reference Method Results
9 Sampling Sheets & Calculations
Data for 9 Laboratory Analyses and Calculations
9 Raw Data sheets documenting H_2O determinations and Calculations
Meter box calibration data & Calculations
Meter box calibration data & Calculations

FIGURE 2-1

Review Process for a Relative Accuracy Test of an SO_2 CEM

Some of the items above may aid the reviewer in validating the test procedures; this is true for the statements of protocol and information provided by the observer. Other sources of information can aid the reviewer in identifying and evaluating anomalous data. In general, the more supplemental information the reviewer has, the more easily the review can be performed, and the more easily and accurately the required level of review can be achieved.

2.2.1 Pretest Protocol Statements

Conducting a monitor performance test is not always straightforward. Many problems can arise which show that there are neither "standard" sources nor "standard" monitors. The nature of the source, monitor, or the monitoring location may require modification of the performance specification test (PST) procedures. In this regard, a fair degree of procedural latitude is permitted in both the Reference Methods and Performance Specifications.

A pretest meeting is often held at which representatives from the agency (usually the observer), the source, and the test team discuss the potential problems associated with the PST and agree upon necessary procedures, modifications, and reporting requirements. The agreed upon procedures are sometimes documented within a pretest protocol statement prepared by either the source or the tester, and the statement may be submitted to the agency. In some cases, the only record of the pretest meeting agreements is the agency representative's notes. Whatever the situation, the reviewer should obtain all documents of pretest procedural decisions and agreements because such information may prove invaluable for the test report review.

2.2.2 The Observer's Notes and Records

Because owners or operators of continuous monitors are required to notify the Administrator no less than 30 days before the monitor operational test period [40 CFR 60.7(a)(5) and 40 CFR 60.13(c)], an observer is usually present during the PST.

If an agency observer is present, a written report and/or observer's checklist may be available. The report/checklist should contain brief summaries of any inconsistencies observed during the test and an estimate of their effect on the test results. Obviously, without having observed the test, the reviewer cannot fully evaluate the validity of the test procedures and raw data. The observer's report may supply the reviewer with valuable supplemental information to facilitate the review and/or aid the reviewer in the review strategy.

2.3 THE LEVEL OF REVIEW

There are three levels of review:

Level I. Cursory check of results.

Level II. Spot check of report.

Level III. Complete review.

In a Level I review, the reviewer checks the results to determine the performance capability of the monitor and confirms that the report contains sufficient raw data to permit a higher level of review. Insufficient data would limit the review to this level.

For Level II, the reviewer recalculates the results of one or more tests from the raw data. The reviewer makes additional checks of the reported data and

procedures using available pretest protocol statements and information provided by the observer.

A Level III review requires considerable effort and a significant time commitment. The reviewer checks all results thoroughly, which may require extensive recalculation, and evaluates all procedures, diagrams, and data using any supplemental information.

In selecting the level of review, there are several factors to consider. The reviewer should consider the importance of the test and the significance of the results. For example, when the accuracy of the values of the reported results is more important than the status of the monitor (i.e., whether the monitor passes or fails the performance test), a Level III effort would be required. The results of a particular part of a performance test, e.g., response time, can also dictate the level of review. For example, when the results of a test conclusively show that the monitor failed the particular part of a performance test, and a glance at the raw data supports this conclusion, further review should be unnecessary. A Level I review, in this case, would suffice.

Supplemental information can also influence the selection of the level of review. If an agency observer has thoroughly documented one or more tests and is satisfied that the results are valid, the reviewer may decide to conduct a Level I review. On the other hand, special tests, e.g., tests to detect or to quantify stratification at the monitoring location, may require additional effort on the part of the reviewer.

The review process is a dynamic activity; the level of review may change between the time the review is initiated and the time it is completed. Thus, the reviewer must be sensitive to the review process and flexible in his approach.

2.4 CONDUCTING THE REVIEW

As the reviewer gains experience, he will probably develop his own review strategies. Two basic guidelines are offered to the novice. First, focus on a manageable part of the report and then proceed from the general to the specific. For instance, in reviewing a relative accuracy test, first check the calculation of the relative accuracy, then validate the reported monitor data from the strip chart records, and finally, validate the reported Reference Method data by recalculating the results from the field and laboratory raw data. This progression from the general to the specific may be terminated at any point corresponding to the selected level of review, or may be terminated upon finding any major discrepancy in the reported data or results. (A major discrepancy is considered any error that affects the performance status of the monitor.)

The following paragraphs present a synopsis of a Level III review. The reviewer is assumed to be well supplied with supplemental information.

(1) The reviewer should check the introductory material of the report against the observer's report and the statements within the pretest protocol and note any discrepancies and evaluate their effect on the results of the test.

(2) The reviewer should examine the results of the test and the discussion of the results, focusing upon those tests that represent borderline cases, i.e., where the monitor is close to the specification, either on the passing side or on the failing side. The order in which the individual tests comprising the PST are reviewed should be decided using this criterion.

(3) Before proceeding to the raw data and calculations, the reviewer should inspect the test report to verify that all the raw data necessary to

recalculate the results are available. Omissions of data should be noted. At the same time, the reviewer should estimate the significance of these omissions with regard to their perceived effect on the reported results.

(4) After identifying data omissions and evaluating their effect on reported results, the reviewer can then recalculate the results. This is the bulk of the task and can require a significant amount of effort. The reviewer should divide the task into workable units and should proceed from the general to the specific. Data should be examined with regard to reasonableness. Here, common sense and experience will, in most cases, suffice in evaluating most of the reported data. For these recalculations, errors and other omissions should be noted, and their effects on the reported results should be evaluated.

(5) When all the procedures, data, calculations, and results have been evaluated, he or she is then in a position to answer the questions:

(a) Has the testing been properly conducted?

(b) Have adequate data been reported to permit a thorough review?

(c) Have all calculations been performed correctly?

(d) What is the status of the monitor as indicated by the data?

2.5 REVIEWER'S REPORT

The reviewer should promptly submit to the source the results of the review. The report should answer the questions listed at the end of Section 2.4. The report should identify those errors, omissions, and inconsistencies that the reviewer feels may have significant effect on the results of the test. Where appropriate, the reviewer should supply corrections and should provide his own

evaluation of the impact of the problems on the results. The reviewer may also recommend future actions.

The report should include the reviewer's evaluation of the status of the monitor, as indicated by the available data, and should reach one of the following conclusions:

(1) The data indicate that the monitor passed the performance specification test;

(2) The data indicate that the monitor failed the performance specification test;

(3) The status of the monitor cannot be determined from the available data.

The second and third conclusions require recommendations. If the monitor failed the PST, the applicable tests should be identified, and appropriate retesting should be recommended. If the status of the monitor cannot be determined, the reviewer should recommend either submission of additional data or retesting.

3.0 TEST REPORT FORMAT

A standardized format for continuous monitor PST reports is highly recommended, because report review can be accomplished more efficiently, effectively, and accurately. In addition, the adoption of standardized reporting requirements that emphasize completeness could promote the application of quality PST procedures. A standardized test reporting format would be beneficial for both agency and source.

In the paragraphs that follow, a report format is recommended. The criteria considered for the development of this recommended format include:

(1) the need for formal elements, such as title pages, certification pages, table of contents, etc.;

(2) the need for background information necessary to present data and results in the proper technical and regulatory perspective; and

(3) the need for sufficient data to determine the performance status of the tested monitor.

The following format reflects minimum, recommended reporting requirements, which are detailed in subsequent sections of this manual. Because minimum reporting requirements are reflected, the format would not apply to all test reporting situations. Rather, the format is a skeleton, which may be added to as necessary, recognizing that PSTs and accompanying test reports are best handled on a case-by-case basis.

The recommended format is first presented in outline form in Figure 3-1; the individual elements are discussed in order of their presentation.

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FIGURE 3-1.

RECOMMENDED

ELEMENTS OF A CONTINUOUS MONITOR

PERFORMANCE TEST REPORT

1.0 Title Page

2.0 Certification Page

3.0 Table of Contents

4.0 Introduction

5.0 Summary of Results

6.0 Discussion of Results

7.0 Description of Source

8.0 Description of Monitors

9.0 Discussion of Testing Procedures

10.0 Performance Testing Data Sheets

Appendices

Appendix I. Reference Method Raw Data

Appendix II. Strip Chart Records

Appendix III. Calibration Data

(1) Title Page

The title page should include the following: (1) identification of the affected facility and its location; (2) the type of pollutant monitor tested (e.g., SO_2 or NO_x monitor); (3) identification of the organization submitting the test report; and (4) the date on which the report was submitted.

(2) Certification Page

For engineering test reports, the test team leader and a professional engineer should verify that the report is accurate and has been reviewed. Review by a professional engineer, however, is not mandatory. The certification page also provides the Agency reviewer with the name of a knowledgeable person to contact in the event that questions arise.

(3) Table of Contents

A table of contents aids the reviewer in locating pertinent sections of the report. The pages of the report should be numbered.

(4) Introduction

The introduction to the test report should include the purpose and background of the test. It should be brief, and the following items should also be included: (1) the name and location of the affected source; (2) a description of the source process (e.g., fossil-fuel fired steam generator); (3) the process production rate (e.g., MW); (4) the fuel category (e.g., bituminous coal); (5) an identification of the regulation(s) requiring monitoring of emissions; (6) if applicable, an identification of the local agency with jurisdiction over the source; (7) a discussion of pertinent pre-test protocol; (8) the names of the testing firm, source, and regulatory

agency observers present during the testing; (9) the types of monitors used (mfg. and model, e.g., Munkus Model 666 SO_2 monitor); and (10) the dates of the operational test period.

(5) Summary of Results

The summary of results is the heart of a monitor test report. It should be tabulated. If the results are juxtaposed with the applicable performance specifications, interpretation and review will be greatly facilitated. Figure 3-2 illustrates an example "Summary of Results."

(6) Discussion of Results

A discussion of the results should follow the summary of results. This discussion should be brief and should focus on those tests in which: (1) anomalous data were obtained, (2) departures from standard test procedures were observed, or (3) failure to meet the performance specification occurred. Possible causes for these anomalies, deviations, and/or failures should be presented and discussed.

(7) Description of Source

The report should contain a brief description of the source, with emphasis on those aspects of source operation that directly affect the monitor performance test. For example, if the source is a fossil-fuel fired steam generator, then the description should address the heat input rate, the fuel, and the location of the monitor within the effluent handling system. The heat input rate determines the necessity for monitoring. The fuel, be it gas, oil, or coal, determines the appropriate continuous monitor span. The continuous monitor location helps to determine the representativeness of the sample. The

FIGURE 3-2
EXAMPLE
SUMMARY OF RESULTS

SO_2 Monitor		Result	Specification
Relative Accuracy		15%	≤20%
Response Time		81 sec	≤15 min
Calibration Error	mid	2%	≤5%
	high	0.4%	≤5%
2-hour Zero Drift		0.3%	≤2%
2-hour Calibration Drift		0.1%	≤2%
24-hour Zero Drift		0.3%	≤2%
24-hour Calibration Drift		1.0%	≤2.5%
Operational Test Period		June 1-7, 1982	≥168h

NO_x Monitor		Result	Specification
Relative Accuracy		37%	≤20%
Response Time		110 sec	≤15 min
Calibration Error	mid	2%	≤5%
	high	2.7%	≤5%
2-hour Zero Drift		0.3%	≤2%
2-hour Calibration Drift		1.7%	≤2%
24-hour Zero Drift		0.2%	≤2%
24-hour Calibration Drift		0.6%	≤2.5%
Operational Test Period		June 1-7, 1982	≥168h

O_2 Monitor	Result	Specification
Response Time	70 sec	≤15 min
2-hour Zero Drift	0.09% O_2	≤0.4% O_2
2-hour Calibration Drift	0.1% O_2	≤0.4% O_2
24-hour Zero Drift	0.1% O_2	≤0.5% O_2
24-hour Calibration Drift	0.1% O_2	≤0.5% O_2
Operational Test Period	June 1-7, 1982	≥168h

location of the monitor (i.e., the region or point within the effluent stream where pollutant emissions are measured) should be addressed within all PST results regardless of the source category.

(8) Monitor Description

The test report should include a brief description of the monitors tested. This is important because, as applied, PST procedures are generally monitor specific. For example, the calibration error tests for extractive and in-situ monitors differ radically. Extractive monitors require injection of calibration gases, while in-situ monitors require the use of cells containing calibration gases. Another example is the measurement basis of the monitor. Moisture measurements must be performed concurrently with reference method determinations during relative accuracy testing of wet basis pollutant gas monitors.

The monitor description should include the following information: (1) the make and model of the monitor; (2) the analytical measurement process (e.g., infrared, second derivative ultraviolet, galvanic concentration cell); (3) the moisture basis (wet or dry); (4) the measurement mode (extractive or in-situ); and (5) the method employed for calibration.

The test report should contain a drawing that illustrates the general locations and relative positions of the monitors and the reference method sampling probe(s) within the effluent handling system (a schematic is acceptable). This drawing serves two purposes. It aids the reviewer in examining anomalous data with reference to process dependent aberrations. Secondly, a drawing will denote proper or improper monitoring and sampling locations.

(9) Discussion of Testing Procedures

The test report should include a section that discusses the procedures employed during the PST. The discussion should be brief and should emphasize those parts of the test for which no established procedures exist and/or those parts of the test in which deviations from established testing procedures occurred. Several examples of procedures that should be discussed are provided below.

When concentrations for calibration gases are determined using the reference methods, procedures for sampling gas cylinders should be described. This is particularly true for Methods 6 and 7, because these methods do not directly apply to high pressure samples. The pertinent sampling procedures should be discussed within the "Testing Procedures" section of the report, or a reference for the procedures should be cited. In the latter case, it would be helpful to include within the report's appendices a copy of the citation that is not readily available.

An analogous example would be the documentation of the method used for determining effluent moisture, if relative accuracy testing was performed for a wet-basis continuous emission monitor. Since Performance Specification 2 does

not prescribe a method for determining moisture, testers may choose among several methodologies. If Reference Method 4 is not used, then the tester must provide a description and discussion of the employed method in the test report. In this regard, Performance Specification 2 explicitly states that the method used for determining moisture and the calculation procedures employed for correcting between differing measurement bases (e.g., wet-basis or dry-basis) are to be reported.

Performance Specification 2 requires the reporting of the method used for obtaining the continuous emission monitor's concentration data for the relative accuracy computation. Therefore, a description of this method should be included within the "Testing Procedures" section of the test report.

Descriptions of monitor-specific PST procedures should also be included within the "Testing Procedures" section. Two such monitor-specific aspects of the PST include:

(1) the pressures and flow rates for calibration gas injections, and

(2) the use of mixed calibration gases, e.g., SO_2 and O_2 in nitrogen, for monitors that have dual analysis capability.

Finally, the "Testing Procedures" section should address all deviations from the reference methods that occurred during the performance program. In this regard, the introductory paragraphs of 40 CFR 60, Appendix A, state:

> ". . . an owner electing to use. . .techniques [cited as 'subject to the approval of the Administrator' or as 'or equivalent'] is responsible for . . .(2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the reference methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application."

(10) Performance Testing Data Sheets

The test report should, as appropriate, contain documentation as specified within Figures 2-1, 2-2, 2-3, 2-4, 2-5, and 2-6 of Performance Specification 2 and within Figures 3-1, 3-2, and 3-3 of Performance Specification 3.

(11) Appendices

The test report should include all the raw data that figured into the PST. In general, these raw data fall into three categories: (a) data from reference method (and moisture) testing, (b) continuous monitor data records, and (c) data from calibration activities.

The reference method (and moisture) raw data should be assembled in one appendix and, as appropriate, should include: sampling data for SO_2, NO_x, and H_2O, and analysis data for SO_2 and NO_x.

Copies of the data recorded by the continuous monitor over the entire operational test period should be included in another appendix.

All calibration data should be included in a separate appendix. These calibration data may derive from pre- and post-test dry gas meter calibrations, thermometer calibrations, and sampling and analysis of SO_2, NO_x, CO_2, and O_2 calibration gases.

Finally, a separate appendix should be included for copies of procedures cited within the "Testing Procedures" section.

4.0 REVIEW OF TEST PROCEDURES, DATA, AND RESULTS OF MONITOR PERFORMANCE TESTS FOR SO_2 AND NO_x MONITORS

This section provides detailed procedures for reviewing the data, calculations, and results of the various monitor performance evaluation tests conducted for SO_2 and NO_x monitors. Included are background information and review procedures for evaluating calibration standards, calibration error tests, conditioning period/operational test period requirements, response time tests, zero and calibration drift tests, and relative accuracy tests. Background information outlining the specific tests and associated procedural requirements is included at the beginning of each subsection.

The procedures presented here provide specific guidelines for review of the reported data and results. In most cases, the recommended review proceeds from a review of the general results to a review of specific data. Example data sheets and calculations are provided for each of the monitor performance evaluation tests.

The performance specifications for pollutant continuous monitors are shown below.

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Parameter	Specification
Accuracy	≤ 20% of the mean value of the reference method test data
Calibration error	≤ 5% of each (50%, 90%) calibration gas mixture value
Zero drift (2 h)[1]	≤ 2% of span
Zero drift (24 h)[1]	≤ 2% of span
Calibration drift (2 h)[1]	≤ 2% of span
Calibration drift (24 h)[1]	≤ 2.5% of span
Response time	≤ 15 min maximum
Operational period	≥ 168 h minimum

[1] Expressed as sum of absolute mean value plus 95% confidence interval of a series of tests.

4.1 CALIBRATION ERROR TEST

4.1.1 Background

The calibration error test for pollutant monitors (SO_2 and NO_x) is a test to determine the accuracy and repeatability of the monitor response relative to calibration standards equivalent to 50% and 90% of the instrument span (normally either 1000 or 1500 ppm). Since the calibration error test involves measurements at 0%, 50%, and 90% of span, this test also provides a check of the linearity of the monitor response over its measurement range.

Performance Specification 2 allows the calibration error test to be performed either in the laboratory or in the field. Thus, the calibration

error test is not necessarily conducted during the operational test period.

Performance Specification 2 states that, for an extractive monitor, three different concentrations of the appropriate pollutant gas must be introduced into the monitoring system: 0%, and "approximately 50% and 90% of span." The performance specification also states that no gas concentration may be introduced twice in succession. The test requires 15 non-consecutive measurements and 5 measurements with each gas. If the monitoring system is non-extractive, the mid- and high-range data are obtained by using gas cells "whose concentrations are certified by the manufacturer to be functionally equivalent to these concentrations."

Performance Specification 2 utilizes only the results from the mid-range (50% span) data and the high-range (90%) data in determining calibration error.

4.1.2 Review of Calibration Error Test Data and Results

The review of the calibration error test should include: (1) a check to verify that the mid-range and high-range calibration errors have been calculated properly from the reported data, (2) a check of the adequacy of test procedures and data obtained, and (3) a verification of the concentration values of the calibration standards employed.

The determination of calibration error employs the same equations for computing differences, mean difference, and confidence interval as does the determination of relative accuracy. (See the example calculations provided in Section 4.5 of this manual.) The mid-range and high-range calibration errors are determined separately from the 5 mid-range and the 5 high-range measurements, respectively. The mean difference must be calculated algebraically (retaining the signs of the differences). The confidence

interval must also be calculated using the algebraic values of the differences. The correct value for $t_{0.975}$ used in the confidence interval calculation is 2.776 for 5 measurements. The calibration error is computed as the sum of the absolute value of the mean of the differences and the confidence interval, divided by the appropriate calibration gas concentration.

Based on the experience of the reviewer and on the particular data set reported, the reviewer must decide either to recalculate the mid-range and/or high-range calibration error results or to accept the reported result. At a minimum, the calibration error test data form should be reviewed for completeness by checking that each calibration point (zero, mid-range, and high-range) is represented by 5 independent measurements. Conformance with specified procedure may be checked by verifying that the datum for each calibration point was obtained in a non-consecutive fashion.

If the calibration error test was conducted during the operational test period, the reviewer should examine the strip charts for consistency between the data reported on the calibration error data form and the values indicated by the charts. Also, the duration of each measurement at 0%, 50%, and 90% of span, as indicated by the strip chart, should be greater than the reported response time of the monitor. This may be difficult to determine visually if, for example, the response time is approximately one minute and the strip chart speed is approximately 1 inch/h. The concentrations of the mid- and high-range calibration gas mixtures should be approximately 50% and 90% of the required instrument span. The reviewer must interpret the acceptable limits established by the word "approximately," since Performance Specification 2 does not elaborate on its meaning. (The October 10, 1979 <u>proposed</u> revisions to Performance Specification 2 require that the high-range gas concentration be

between 80% and 90% of span, and that the mid-range gas concentration be between 45% and 55% of the span.)

The interpretation of the recorded responses to zero gas injections must be approached with caution, because anomalous data may reflect the test technique, fundamental limitations of the monitor, or impending monitor malfunction. Without a firm understanding of monitor operation, it is generally difficult to draw valid conclusions about monitor performance from what appear to be anomalous zero data.

The actual values of the calibration standards employed directly affect the outcome of the calibration error test. Errors in the values of the calibration gases cannot be distinguished from monitor non-linearity in the results of the calibration error test. Thus, the true concentration values of the calibration gases or functionally equivalent concentrations of calibration cells must be determined. The reviewer is directed to Section 4.5.4.4 of this manual, where guidelines for checking reported calibration standard values are provided.

4.2 CONDITIONING PERIOD; OPERATIONAL TEST PERIOD

4.2.1 Background

Performance Specification 2 requires that pollutant continuous emission monitors be operated for an initial 168-hour conditioning period in a normal operating manner. The strip chart recorder should be offset approximately 10% during the conditioning period to facilitate observation of negative drift. At a minimum, the "normal operating manner" requires that the monitor zero and span be checked daily, and that the monitor operate continuously over the 168-hour period. Monitor failure during the conditioning period requires

reinitiation of the conditioning period once the monitor is repaired. In contrast, if the source shuts down during the conditioning period, then the 168-hour period is interrupted and then is continued when the source resumes operation.

The 168-hour operational test period is conducted after the conditioning period is completed. The operational test period need not immediately follow the conditioning period. During the operational test period, the response time test, relative accuracy test, and zero and calibration drift tests are conducted. The calibration error test is most often conducted in the field during the operational test period; however, as pointed out in Section 3.2.1, Performance Specification 2 permits the accomplishment of this test in the laboratory also.

During the operational test period, the continuous monitor must continuously monitor the effluent, and the data recorder zero should be offset approximately 10%. Performance Specification 2 states, "during the 168-hour operational test period, the continuous monitor shall not require any corrective maintenance, repair, replacement, or adjustment other than that clearly specified as required in the operation and maintenance manuals as routine and expected during a one-week period."

4.2.2 Review of Operational Test Period

The strip chart records (or computer printouts) for the operational test period should be included in the test report. The reviewer should check the data record to ensure that the requirements of the operational test period are met.

The source of the monitoring raw data obtained during the operational test period is usually strip chart records. These records must be accurately and extensively documented. Furthermore, copies of the strip charts included in the report must be of high quality. If these conditions are not met, it is often neither cost effective nor possible to check the accuracy of the reported monitor data.

Dates and clock times should be accurately documented on the charts. The time should be indicated either on a 24-hour basis or labelled with either PM or AM. (Chart paper is available printed with clock times; however, such paper does not guarantee the accuracy of the printed times.) At least once daily, the chart should be labelled with the appropriate date - including year. In addition, all pertinent traces should be marked to indicate the clock time. Such marking will ensure that the chart recorder is chronologically accurate.

The identification and description of the concentration-dependent axis must be precise and complete if the chart is to be interpreted correctly. This should include: (1) the span indicated by the chart paper both with and without the 10% zero offset; and (2) an indication of whether a zero offset is present. The reasoning behind these reporting requirements can be illlustrated with the following example. If the chart has a 1000 ppm span, and the zero is offset 10%, then the new span could either become 900 ppm (the entire range was shifted) or remain at 1000 ppm (the entire scale was proportionally reduced). This problem can often be resolved by investigating the responses observed during monitor calibration, but this is not always possible, especially when only poor copies of the strip charts are available.

All pertinent traces should be identified. An often overlooked problem with strip chart documentation is the identification of traces by pen color:

this information is not translated by black and white copy.

The reviewer should watch for disparities between reported and recorded times; this may indicate problems with chart speed control. Variations in chart speed can be determined by measuring time intervals with a rule.

Those traces corresponding to tests for response, calibration error, and drifts should be clearly identifed on the strip charts. Most important, the strip chart should be marked to indicate those time periods that supplied the data for the relative accuracy computation.

Other explainable variations in monitor response (e.g., unusual monitor responses observed while the test team initially establishes the proper calibration gas flow rates/injection pressures) should also be clearly identified to prevent misinterpretation of these events as monitor failures. Other than the above instances, the continuous monitor should provide an uninterrupted data record for the entire operational test period. Data records indicating unexplained periods of zero readings, offscale readings, exactly constant readings, or widely fluctuating emission values should be considered suspect by the reviewer, because they suggest instrument malfunction.

4.3 RESPONSE TIME TEST

4.3.1 Background

The continuous monitoring requirements of 40 CFR 60.13(e)(2) state, "All continuous monitoring systems ... for measuring oxides of nitrogen [and] sulfur dioxide ... shall complete a minimum of one cycle of operation (sampling, analyzing, and data recording) for each successive 15 minute period." To ensure that this requirement is met, Performance Specification 2 limits monitor response time to 15 minutes and defines response time as, "the time interval from a step change in pollutant concentration at the input to the continuous monitoring system to the time at which 95 percent of the corresponding final value is reached as displayed on the continuous monitoring system data recorder." It is important to note that the regulations clearly indicate that the response time test is intended to include the entire monitoring system.

For response time tests performed on extractive monitors, gases representing 0% and 90% of the applicable span concentration are introduced into the monitor in sequential order, and the times required for the monitor to attain 95% of the resultant step changes are recorded. Both upscale and downscale responses are measured three times each. This is readily accomplished by alternately switching from zero to span conditions. The response time for a particular step change is the average of the three measurements, and the reported monitor response time is the slower of the two average response times.

The calculation procedures of Performance Specification 2 (Paragraph 7.2.1), as distinguished from the performance specifications contained in Table 2-1, address the matter of differing upscale and downscale response times; a

maximum difference of 15% relative to the slower response time is specified.

The response time test procedures of extractive and non-extractive (in-situ) continuous monitoring systems are not the same. For response time tests of non-extractive monitors, the analyzer is evaluated with respect to a calibration gas cell and a simulated zero condition. The resultant analyzer response time is predominately dependent on the time required for the cells to be placed within the light path of the analyzer. (Most non-extractive monitors use the attenuation of electromagnetic radiation, i.e., infrared, ultraviolet, etc., for determining the concentration of a pollutant specie.) The total response time of a non-extractive monitoring system may also be dependent on whether the analyzer provides instantaneous or integrated values and whether the analyzer serves to monitor more than one pollutant (or diluent) gas. For example, many in-situ monitors are designed with "sample and hold" circuitry to display integrated sampling values. In this situation, the monitor must complete a full integration cycle before a new emission value is displayed. Also, some in-situ systems monitor more than one pollutant; alternating, for example, between SO_2 and NO_x for short intervals.

The operation of extractive monitors, on the other hand, requires the transport of the effluent sample to the analyzer. The process of transporting the sample takes a finite amount of time, which is dependent on the flow rate of the sampling system and the length of the sampling line. Consequently, extractive monitors generally show a delay between the time of sample acquisition and the time of analysis and recording.

To a large degree, measured response times of extractive continuous emission monitors reflect the time demanded by sample transport. In this regard the reviewer should recognize that the length of connections between gas

cylinders and the tested monitor can affect the response time test result if these connections are inordinately long. For well calibrated extractive monitors, failure to meet the response time specification is rare, and when failure does occur it most frequently is a result of inappropriate testing technique.

For extractive monitors, response time also may be lengthened because of physicochemical interactions, such as adsorption or desorption of the pollutant on or from the sampling interface and/or dissolving and degassing of the pollutant to or from liquid phases. These effects are dependent on the duration of the response time tests, the span gas concentration, and the sampling history of the monitor. Physicochemical interactions can manifest themselves as widely differing response times for the upscale and downscale responses. Such problems, however, are generally encountered during calibration error testing, if such testing is performed in the field.

Finally, for some extractive monitoring systems, a single analyzer may monitor several sampling locations; the analyzer is time-shared between the various sampling locations. The time required to complete a full sampling cycle, which includes all sampling locations, should be included in the reported response time.

4.3.2 Review of Response Time Test Data Sheet and Strip Chart Records

The small amount of data generated for a response time test makes the review straightforward and relatively easy. The reviewer should confirm the following: (1) the reported span gas concentration is "approximately" 90% of the applicable span, (2) three upscale and three downscale response time tests

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Figure 4-1
Example Data for RESPONSE TIME Test

Plant and location Amalgamated Mung, Inc. Unit #3

Monitor SO_2 Monitor

Date of test 2/26/79

Span gas concentration 1290 ppm ← Value should be 90% of span for extractive monitor. For in situ monitors, highest available cell concentration.

Monitor span setting 1500 ppm ← Determined by nature of source.

Upscale Response
1 75 seconds
2 71 seconds
3 77 seconds
4 _____ seconds
5 _____ seconds
} 3 measurements?

Avg. Upscale Response 74 seconds } Avg. computed correctly?

Downscale Response
1 81 seconds
2 83 seconds
3 79 seconds
4 _____ seconds
5 _____ seconds
} 3 measurements?

Avg. Downscale Response 81 seconds } Avg. computed correctly?

System response time (slower time) = 81 seconds Slower response time?

Percent deviation from slower system average response = $\left[\frac{\text{(average upscale) - (average downscale)}}{\text{slower time}}\right] \times 100 =$ 0 %

Correctly calculated? →

are reported, (3) the reported values for the average response times (upscale and downscale) are correct, (4) the reported system average response time is the longer average response time, and (5) the value reported for the "percent deviation from slower system average response" is correct. The reported response time is intended to reflect the response time for the entire monitoring system. It includes the full sampling cycle time if the monitor samples multiple gases or at multiple locations.

Performance Specification 2 limits average response times (upscale and downscale) to a maximum of 15 minutes (900 seconds). An additional limit is placed on the percentage difference between the average response times; the percentage deviation of the two response times, relative to the slower average response time, must be less than or equal to 15%. This is summarized by the following formula:

$$\%\ \text{deviation from slower system average response} = \frac{\left[\text{average upscale response time} - \text{average downscale response time}\right]}{\text{slower average response time}} \times 100\%$$

This latter specification (Paragraph 7.2.7, Performance Specification 2) is not listed with the monitor performance specifications that appear in Table 2-1 of Performance Specification 2.

In the limit of fast response times, the specification regarding percentage deviation can cause interpretive problems outside the intent of Performance Specification 2. For example, if the average upscale response is 25 seconds, and the average downscale response is 30 seconds, the percentage deviation is 17%. In this example, the monitor response is very fast compared

to the 15-minute response time specification, but the monitor fails the specification for percentage deviation. Obviously, this is not the intent of the percent deviation specification. Accordingly, the proposed revisions (October 10, 1979) address only the slower response time.

The reviewer may attempt to verify the reported response times by consulting the appropriate strip chart records. The strip charts should bear the following information: chart speed, labelled points marking the initiation of each response time test, and labelled points marking the positions of all maximum deflections. In most cases, reviewing the strip chart records entails either visual inspection or an approximation with a rule, depending on the response time of the monitoring system.

In those cases in which the reported response times are close to the 15-minute limit and in which the final value is approached asymptotically, the strip chart records should be checked with a rule. The most commonly encountered problem in attempting to verify the reported response time is either that the point marking the initiation of the concentration step change is not labelled on the strip chart or that the times for gas injections are not contained on the data sheets. This situation prevents the reviewer from verifying the response time data.

There are situations in which the reviewer will be unable to obtain the response times from the strip charts. For example, if the response time of a monitor is very fast relative to the chart speed, the response time test will appear as a spike on the paper. Although the monitor response time cannot usually be determined from these records, it is often evident that the monitor meets the response time specification. The strip chart records serve only to document that the response time test was conducted.

If the strip chart is accurately documented and if the trace shows three uniformly spaced pairs of alternating upscale and downscale responses within a time period significantly less than 90 minutes (i.e., 15 minute response time test x 6 tests), it is reasonable to presume that the monitor meets the response time specification.

4.4 ZERO AND CALIBRATION DRIFT TESTS

4.4.1 Background

The drift tests described in Performance Specification 2 provide estimates of the temporal stability of the monitor's calibration. The zero and calibration drifts are determined by two independent tests: the 2-hour zero and calibration drift test, and the 24-hour zero and calibration drift test.

For extractive monitoring systems, the drift tests involve introducing zero and span gases into the monitoring system. For in-situ monitoring systems that cannot accept calibration gases, a calibration gas cell "functionally equivalent to 50 percent of span concentration" is used in lieu of span gas. In addition, such in-situ monitors must have some means of producing a "zero condition that provides a system check of the analyzer internal mirrors and all electronic circuitry including the radiation source and the detector assembly." The performance specification permits an extrapolative method as an alternative to simulating a zero condition, if the monitor lacks direct zeroing ability. For example, three or more calibration gas cells are inserted in the monitor, and extrapolation from these values provides the zero response. Owners or operators of these monitors are required to retain a graph which illustrates the extrapolation operation. The validity of this extrapolative technique is based upon the following assumptions: (1) the monitor response over the entire range of extrapolation can be described by a linear equation; (2) the three or more points are well spaced over the instrument's measurement range; (3) the concentrations of the gas cells are known to a high degree of accuracy; and (4) the extrapolation to the zero value is not affected by span drift. Evaluation of these extrapolative procedures must be conducted on a case-by-case basis.

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4.4.1.1 2-Hour Drift Test

The 2-hour zero and calibration drift tests require 15 data sets collected at 2-hour intervals. This particular test is intended to quantify drift on a short term basis. For example, the test is capable of identifying diurnal variations in monitor response.

The important data obtained from the 2-hour drift tests are the differences between consecutive zero and span measurements. Adjustments to the monitor during the 2-hour drift tests are not allowed. A minimum of 16 data sets of zero and span measurements should be acquired, because 15 differences, determined at 2-hour intervals, are required for the test. Thus, the first data set is the starting point for obtaining the first difference data.

The data are not allowed to represent non-consecutive measurements; thus, in the event that a series of 2-hour determinations is interrupted, a new set of data must be generated as a starting point before more difference data may be obtained.

4.4.1.2 24-Hour Drift Tests

The purpose of the 24-hour drift tests is to reveal variations in monitor calibration which may occur on a day-to-day basis. Measurements are conducted at 24-hour intervals until 7 drift determinations are obtained. Since 8 consecutive sets of zero and span readings are necessary to provide 7 drift determinations, the 24-hour zero and calibration drift tests normally define the time of the operational test period.

According to Performance Specification 2, manual adjustments to the monitor during the 24-hour drift tests are permitted only at 24-hour intervals,

unless the monitor manufacturer specifies a shorter interval for manual adjustments. Automatic adjustments, on the other hand, are allowed at any time. Specifically, the 24-hour drift tests require the following procedure at 24-hour intervals: (1) measurement of the zero value; (2) adjustment of the zero response to the correct value, if necessary; (3) measurement of the span value; and (4) adjustment of the span response to the correct value, if necessary. The chart recorder zero value must be sufficiently offset during the tests, to allow for the determination of negative drift. Performance Specification 2 states that the offset should be approximately 10%. However, for practical reasons smaller offsets may be validly employed as long as all drifts are recorded on scale.

Some monitor vendors suggest that the adjustments not be made at 24-hour intervals; they would rather allow the drift to accumulate for the entire operational test period, provided that the total drift does not exceed the respective performance specification drift limitations. If this procedure is employed, then the 24-hour zero and calibration drift values should be calculated in the same manner as in the 2-hour drift tests.

For the 24-hour drift tests, the zero is adjusted after the zero measurement but before the span measurement. Consequently, the procedure for conducting the 24-hour drift tests automatically removes the effects of zero drift from the span measurements. The measured span drifts are, therefore, equivalent to calibration drifts, and no further manipulation of the data is required.

4.4.2 Review of Zero and Calibration Drift Tests

In reviewing the drift test data and results for both the 2-hour and 24-hour tests the reviewer should perform the following checks: (1) check the

Figure 4-2

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2 HOUR ZERO AND CALIBRATION DRIFT
Example Data

Source and Location Amalgamated Mung, Inc., Unit #3

Monitor Munkus SO_2 Monitor

Data Set No.	Time Begin	Time End	Date	Zero Reading	Zero Drift (Δ Zero)	90% Span? Span Reading	Span Drift (Δ Span)	Calibration Drift (Span − Zero)	
1	1000	1005	2/29	0	* −	1285	* −	* −	
2	1200	1205	"	−4	−4	1281	−4	0	1
3	1400	1405	"	−3	+1	1280	−1	−2	2
4	1600	1605	"	−1	+2	1282	+2	0	3
5	1800	1805	"	+1	+2	1282	0	−2	4
6	1000	1005	2/30	+2	* −	1284	* −	* −	
7	1200	1205	"	0	−2	1287	+3	+5	5
8	1400	1405	"	0	0	1286	−1	−1	6
9	1600	1605	"	0	0	1287	+1	+1	7
10	1800	1805	"	−1	−1	1285	−2	−1	8
11	0800	0805	2/31	0	* −	1286	* −	* −	
12	1000	1005	"	+3	+3	1289	+3	0	9
13	1200	1205	"	+2	−1	1289	0	+1	10
14	1400	1405	"	+1	−1	1287	−2	−1	11
15	1600	1605	"	+1	0	1286	−1	−1	12
16	1400	1405	3/1	−13	* −	1283	* −	* −	
17	1600	1605	"	+10	+23	1297	+14	−7	13
18	1800	1805	"	+5	−5	1324	+27	+32	14
19	2000	2005	"	+8	+3	1314	−10	−13	15
20									
21									
22									
23									
24									

e.g. $8 - 5 = 3$; $1314 - 1324 = -10$; $(-10) - (+3) = -13$

Two-hour intervals between data sets?

15 drift determinations? * 19 data sets required here because of interruptions.

Zero Drift = [Mean Zero Drift* 1.333 + C.I. (Zero) 3.556]

÷ [Instrument Span] x 100 = ~~3.2%~~. 0.3%

Calibration Drift = [Mean Span Drift* 0.733 + C.I. (Span) 5.281]

÷ [Instrument Span] x 100 = 0.4%.

* Absolute value

Have these calculations been performed correctly?

$t^{15}_{0.975} = 2.145$, Instrument Span = 1500 ppm

concentration value of the calibration gas or calibration gas cell used to span the monitor, (2) check for the required number of zero and span measurements, (3) check the individual zero and calibration drift calculations, (4) check the reported zero and calibration drift determinations against the individual drift measurements, and (5) check the values recorded on the data sheet against the strip chart records.

4.4.2.1 2-Hour Drift Tests

For extractive monitors, the 90% of span calibration gas is specified for use in the 2-hour drift tests. For non-extractive monitoring systems, the calibration gas cell is specified to be equivalent to 50% of span. The reviewer should check the report for conformance with these specifications.

The 2-hour drift tests require 15 sets of drift determinations, in which each data set is composed of initial and final zero and span readings. Consecutive drift determinations may utilize the same data set (i.e., a particular zero and span value can be used as the final measurements in one drift determination and as the initial measurements in the following drift determination). Thus, at a minimum, 16 sets of zero and span measurements must be acquired. An additional set of measurements is required each time the drift test sequence is interrupted. It should be noted that 2-hour drift testing may span and even include the time period when 24-hour drift measurements are made, as long as no adjustments to the monitor are performed during the 24-hour drift test for that particular day. If, on the other hand, adjustments occur during the affected 24-hour drift test, then the 2-hour drift testing is interrupted and the testing sequence must be reinitiated.

Deviations from exact 2-hour timing are not uncommon. Because Performance Specification 2 does not address this subject, the significance of timing deviations must be assessed on a case-by-case basis by the reviewer. In this regard, it is recommended that the reviewer base his judgement on whether the drift data indicate that the monitor's calibration is stable over short time periods.

For each drift determination (initial and final zero and span measurements), the zero drift is determined as the final zero reading minus the initial zero reading. Similarly, the span drift is determined as the final span reading minus the initial span reading. The calibration drift is then determined as the span drift minus the zero drift. The reviewer should check to see that the above subtractions are performed consistently, and that algebraic values are employed in determining the calibration drift.

The mean zero drift is determined from the algebraic sum (retaining signs) of the 15 zero drift determinations. The confidence interval for the zero drift test is also calculated by employing algebraic values of the measured zero drifts. The value of $t_{0.975}$ for use in the confidence interval calculation is 2.145 for 15 measurements. (A detailed example confidence interval calculation is included in the "Review of Relative Accuracy Calculations" section of this manual.) The reported 2-hour zero drift should be calculated as:

$$\text{zero drift} = \frac{\left|\text{Mean Zero Drift}\right| + \text{Confidence Interval}}{\text{Instrument Span}} \times 100$$

The reported 2-hour calibration drift is determined from the 15 calibration drift determinations in exactly the same manner as the zero drift is calculated.

4.4.2.2 24-Hour Drift Tests

The review of the 24-hour zero and calibration drift tests is very similar to the review of the 2-hour drift tests. The same requirements apply to the value of the calibration standard used to span the system for both drift tests. The value of the zero offset employed should also be determined before reviewing data acquired from the strip chart records.

The 24-hour drift test requires 8 sets of zero and span measurements to facilitate 7 zero and calibration drift determinations. The procedure prescribed by Performance Specification 2 requires adjustments to the zero and span values following the respective zero and span measurements. Provided that this procedure is followed, the individual zero drift values are calculated as the zero value measured at the end of the 24-hour interval, minus the correct zero value. In the same manner, the calibration drift is the span value at the end of the 24-hour interval minus the correct span value. The adjustment of the zero value after the zero reading and before the span reading automatically removes the effects of zero drift on the span measurements. Thus, no further correction of the span measurements is necessary.

For reasons discussed in Section 4.4.1.2, rather than performing the 24-hour zero and span adjustments, testers often allow drift to accumulate. If this procedure is employed, the 24-hour zero and calibration drifts are determined in exactly the same manner as for the 2-hour drift tests.

The calculation procedure for determining the reported 24-hour zero and calibration drifts from the individual drift measurements is the same as that described for the 2-hour drift tests. The mean zero drift, mean calibration drift, and respective confidence intervals are determined using algebraic values. (Pertinent, detailed example calculations are included in the "Review of Relative Accuracy Calculations" section of this manual.) The value of $t_{0.975}$ for use in the confidence interval calculation is 2.447 for 7 drift determinations. The reported 24-hour zero and calibration drifts are computed as:

$$\begin{matrix}\text{zero drift} \\ \text{or} \\ \text{span drift}\end{matrix} = \frac{\left|\begin{matrix}\text{Mean Zero Drift} \\ \text{or} \\ \text{Mean Span Drift}\end{matrix}\right| + \text{Confidence Interval}}{\text{Instrument Span}} \times 100$$

4.4.3 Review of 2-Hour and 24-Hour Drift Test Strip Chart Records

The reviewer should confirm the accuracy of the span and zero values reported in the drift test data sheets by comparing them with corresponding values on the strip chart record. In addition, the reviewer should verify that all drift traces are on scale. Traces which reflect pegging at either end of the strip chart will necessarily invalidate a drift test, because the true magnitude of the pegged response cannot be determined. Finally, the reviewer should check that the times reported on the data sheet match the times indicated on the strip chart recording for the zero and span measurements.

4.5 RELATIVE ACCURACY TEST

4.5.1 Background

The relative accuracy test is performed to assess the adequacy of the calibration technique of the continuous monitor. The test entails the comparison of pollutant concentrations determined by the continuous monitor to concentrations concurrently determined by EPA Reference Methods 6 and/or 7. When relative accuracy tests are conducted on continuous monitors that measure pollutant concentration on a wet basis, these two reference methods must be suplemented by an Agency approved method for determining the effluent stream moisture content. The result from the moisture determination is used to place all the effluent measurements on a consistent moisture basis.

The reported relative accuracy result is calculated from three terms. One term is the algebraic mean difference observed between the monitor and reference method concentration measurements. This mean difference term may be interpreted as the absolute bias or inaccuracy of the monitor measurements. A second term, the 95% confidence interval, is the precision estimate associated with the determination of the mean difference. The remaining term used in the computation is the mean concentration of the reference method determinations. The sum of the confidence interval and the absolute value of the mean difference divided by the mean reference method concentration, affords the relative accuracy which is expressed as a percentage.

Performance Specification 2 calls for 9 Method 6 measurements when tests are conducted to determine the relative accuracy of an SO_2 monitor. A determination of the relative accuracy of an NO_x monitor likewise requires 9 measurements of the pollutant concentration, but in this case each measurement is the average of three Method 7 determinations each conducted over

approximately three minute intervals. Thus, 27 determinations of the NO_x concentration in the effluent are required for the relative accuracy test.

Since the determination of relative accuracy involves a considerable amount of reference method sampling and analysis, the amount of attendant data is exceptionally large, relative to the other monitor performance tests. The effort required in reviewing relative accuracy tests is likewise increased proportionally.

The review of the relative accuracy test can be divided into several major areas: (1) review of the relative accuracy calculations; (2) determination of continuous monitor values; and (3) review of reference method sampling data and results. The following subsections in this report treat each of these topics separately.

4.5.2 Review of Relative Accuracy Calculations

The most common error in monitor performance evaluation test reports is the incorrect calculation of relative accuracy from the reported data. Therefore, if there is any doubt about the value reported for relative accuracy, the reviewer should perform the entire calculation as a check. Because of the frequency of this error, a detailed discussion and an example of the relative accuracy computation are provided below.

The reviewer should first check the relative accuracy data form for the 9 data sets, required as the minimum number of sampling runs by Performance Specification 2. In many cases, a reference sample is inadvertently lost or invalidated. This situation is not uncommon because much sampling is involved: 9 SO_2 samples; 27 NO_x samples; and in some cases, 9 H_2O samples. The reviewer may decide to accept less than 9 data sets, provided the results clearly

indicate compliance with (or failure of) the relative accuracy specification.

The review of the relative accuracy test data form should next focus on the times reported for the reference method sampling. Performance Specification 2 states that no more than one run may be conducted in any one hour. The interpretation of this requirement calls for flexibility. Deviations of several minutes do not violate the intent of this specification.

The reviewer should verify that the monitor and the concurrent reference method values are accurately reported and the differences have been determined accurately. According to Performance Specification 2, these differences are computed by subtracting the reference method value from the concurrent monitor value. Thus, positive differences arise when the monitor reads higher than the reference method values. There will be no effect on the value of the calculated relative accuracy result if the subtraction operation is performed in the reverse manner, provided the subtraction operation is performed consistently throughout the calculation. However, the interpretation of the individual data is reversed if the subtraction operation is reversed, i.e., negative differences will occur when the monitor reads higher than the reference method sampling results.

After checking that the differences are correctly determined, the reviewer should compute the mean reference method value, the mean of the differences, the confidence interval, and finally, the relative accuracy.

(1) Mean Reference Method Value

The mean Reference Method value is simply the arithmetic average of the 9 reported pollutant determination results. It is employed in the denominator of the relative accuracy calculation to express the accuracy on a relative basis.

Figure 4-4

Example Data

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ACCURACY DETERMINATION (SO_2 AND NO_x)

Source and Location Amalgamated Mung, Inc. Unit #3 Stack

Monitor NO Monitor

Nine runs? One run per hour?

Differences consistently calculated?

Test No.	Date & Time	Reference Method Samples SO_2 #1 (ppm)	NO_x #1 (ppm)	NO_x #2 (ppm)	NO_x #3 (ppm)	NO_x avg (ppm)	Monitor Avg. (ppm)* SO_2	Monitor Avg. (ppm)* NO_x	Difference (ppm) SO_2	Difference (ppm) NO_x
1	2/27/79 1025		224	225	222	224		304		80
2	" 1125		214	213	209	212		296		82
3	" 1230		202	198	196	199		262		60
4	" 1333		222	212	218	217		265		43
5	" 1433		229	224	218	224		272		43
6	" 1531		213	217	216	215		296		83
7	" 1635		223	223	216	221		282		61
8	2/28/79 0955		213	223	214	217		302		89
9	" 1104		234	237	235	235		309		75
10										
11										
12										

3 samples per run?

Are averages correct?

Consistent Moisture Basis?

Mean ref. method test value (SO_2) _____

Mean ref. method test value (NO_x) 218

Mean of the differences 68

95% Confidence intervals = ± _____ ppm (SO_2), = ± 13 ppm (NO_x)

$$\text{Accuracies} = \frac{\text{Mean of the differences} \mid + \text{95\% confidence interval}}{\text{Mean reference method value}} \times 100 =$$

_____ %(SO_2), = 37 %(NO_x).

* Explain and report method used to determine integrated averages

$t_{0.975}^{9} = 2.306$

Have the calculations above been performed correctly?

(2) Absolute Value of the Mean of the Differences

The algebraic differences between concurrent Reference Method values and monitor values are summed and averaged. Summing algebraic values requires the retention of the sign of the differences. Consequently, the computed mean difference may be a negative or positive number, or even zero. (It should be noted that the sum of the differences result also enters into the calculation of the 95% confidence interval, and therefore, repetitive calculations can be avoided by recording this value for later use.)

(3) The 95% Confidence Interval ($C.I._{0.95}$)

The determination of the 95% confidence interval is the greatest source of error. The formula used in the determination is given by:

$$C.I._{0.95} = \frac{t_{0.975}}{n\sqrt{n-1}} \sqrt{n\,(\Sigma x_i^2) - (\Sigma x_i)^2}$$

Where:

$C.I._{0.95}$ = 95 percent confidence interval;

n = number of data points (In this example, n = 9);

x_i = algebraic value of a measurement (Some versions of the performance specifications define x as the absolute value of a measurement; this is not correct.)

Σx_i = sum of the n measurements;

$t_{0.975}$ = t score for checking both upper and lower limits its with 95 percent certainty, corrected for n degrees of freedom.

For the relative accuracy test, the operations required for the calculation of the confidence interval apply strictly to the data represented by the differences. Again, attention should be placed on summing algebraic values (as opposed to absolute values) in computations of the 95% confidence interval.

A common error in the calculation of the 95% confidence interval is the use of an incorrect $t_{0.975}$ value. The reviewer should verify that the calculation employs the correct value. In the majority of cases, the error is the result of the use of an adjacent value from the tabulated t scores ($t_{0.975}$). A detailed example confidence interval calculation is provided in Figure 4-5.

(4) Relative Accuracy

The reported relative accuracy should be calculated as:

$$\text{Relative Accuracy} = \frac{\left|\text{Mean of Differences}\right| + C.I._{0.95}}{\text{Mean Reference Method Value}} \times 100$$

It should be emphasized that the absolute value of the mean of the differences is used in calculating the relative accuracy. As a final step, the reviewer should check that the calculated relative accuracy value is the same as the value listed in the "Summary of Results" section of the test report.

Figure 4-5
Example Confidence Interval Calculation

Differences

	x_i	x_i^2
1	26	676
2	-32	1024
3	-71	5041
4	-90	8100
5	-45	2025
6	-75	5625
7	-31	961
8	-17	289
9	-23	529

$$\sum x_i = -296 \qquad \sum x_i^2 = 24270$$

95% Confidence Interval = $CI_{.95}$

$$CI_{.95} = \frac{t_{0.975}}{n\sqrt{n-1}} \sqrt{n\left(\sum x_i^2\right) - \left(\sum x_i\right)^2}$$

$t_{0.975} = 2.306$ for $n = 9$

$$CI_{.95} = \frac{2.306}{9\sqrt{9-1}} \sqrt{9(24270) - (-296)^2}$$

$$CI_{.95} = \frac{2.306}{9 \times 2.828} \sqrt{218430 - 87616}$$

$$CI_{.95} = 32.79$$

4.5.3 Determinations of Continuous Monitor System Values

The relative accuracy test entails comparing the concentrations determined by the continuous monitor to concentrations determined by the reference method.

The following factors should be considered when quantifying the continuous monitor system measurements from the chart records: (1) the time interval (duration) for comparison of monitor system data to sampling data, (2) the method of integrating or averaging the continuous monitor system data, and (3) the response time of the monitor system.

Performance Specification 2, (Paragraph 7.2.1) requires the continuous monitor data to be determined by integrating or averaging the pollutant concentrations over each of the time intervals concurrent with each reference method testing period. The data form (Figure 2-3) provided in Performance Specification 2 indicates that an hourly average of the pollutant concentration should be used for comparison with reference method data. However, it is generally recognized that this hourly averaging note is inconsistent with the sampling times observed for EPA Methods 6 and 7: 20 minutes and approximately 3 minutes, respectively. Accordingly, the average concentration measured by the monitor ordinarily is determined over time intervals corresponding to reference method sampling times.

If strip chart records served as the source for the average monitor concentrations obtained during the relative accuracy determinations, those portions of the trace corresponding to the tests should be bracketed and labelled according to run number.

The method of integrating or averaging the continuous monitor system output over the time interval corresponding to the reference method tests may

affect the accuracy determination. If the monitoring system provides a numerical output or integrated averages, then the problem is usually not significant. However, equal intervals must be used to average the data. If the monitoring system provides a continuous record (strip chart), then averaging the data may be more difficult, particularly where large variations in the pollutant concentration with time are encountered. In this situation, taking as many readings as the resolution of the data record permits and averaging the readings may provide good results.

In many cases, the strip chart record can be integrated by simple visual inspection.

Performance Specification 2 states that the method for performing this integration is to be reported. The reviewer should check that the reported method can be applied to the monitoring data record to afford results equivalent to those contained in the relative accuracy test data sheet. The reviewer may find that the method for determining the integrated averages is not reported. In addition, cases may arise when disparities occur between the recorded averages and the reported averages. For both these possibilities, the reviewer should weigh the significance of the report deficiencies against the impact of these deficiencies on the relative accuracy result. For example, if the relative accuracy result would change from 7% to 13% as a consequence of errors in figuring the integrated averages from the continuous emission data monitor record, the change would be considered insignificant because indicated performance is unchanged relative to the specification $\leq$ 20%.

4.5.4 Review of Reference Method Data and Results

This section details the review of the reference method sampling results employed in the relative accuracy determination. In this portion of the monitor performance test review, the reviewer attempts to accomplish several objectives: (1) to determine whether appropriate sampling and analytical procedures were employed; (2) to determine whether sufficient data are included in the documentation of the testing; (3) to verify the accuracy and correctness of calculation procedures employed in determining the final test results; and (4) where possible, to establish the validity of the data and results by comparison with other parameters, e.g., fuel analysis data.

The agency observer bears the primary responsibility for ensuring that proper testing procedures were employed. If an agency observer was present during the monitor performance test, then the observer's report and field notes should be reviewed and compared with the data and results from the reference method sampling.

The reviewer cannot always ascertain that correct sampling and analytical procedures were employed. In some cases, the range of values for particular data or intermediate results can be bracketed. Results or data that fall outside of reasonable and normal ranges require additional scrutiny. The skilled reviewer is often able to determine quickly which parts of the sampling data and results require a closer check or additional documentation.

The following subsections treat the subjects of SO_2, NO_x, and moisture determinations separately. Background information for the novice reviewer and procedures for reviewing field sampling data, laboratory analytical results, and calculations of gas concentrations are included in each section, as appropriate.

4.5.4.1 Reference Method 6 - SO_2

Background

EPA Reference Method 6 is specified for determining dry basis SO_2 concentrations in stationary source effluent streams. The application of the method essentially entails sampling a measured volume of the effluent through impingers containing hydrogen peroxide where SO_2 quantitatively reacts to sulfate ion, which is determined titrimetrically using the barium-thorin method. When applied to monitor relative accuracy tests, Reference Method 6 sampling is conducted with the probe positioned adjacent to the monitor's probe. This positioning ensures that the comparative results will be based upon measurements performed on equivalent samples. The barium-thorin method does not necessitate a laboratory environment; consequently titrations are often conducted in the field.

Review of Field Sampling Data

Raw data sheets documenting the Reference Method 6 sampling should be included in the monitor test report. Data sheets should be included for all of the sampling runs reported on the relative accuracy data sheet. The reviewer should check these data to ensure that the required sampling procedures were followed, that sufficient data were reported, and that the reported data are within reasonable ranges. Each raw data sheet should provide the information necessary to calculate the volume of effluent sampled, corrected to dry standard conditions. This volume, in conjunction with the laboratory analytical data, is used to calculate the SO_2 concentration of the sample.

Each raw data sheet should contain the following identifying information (see example sheet): (1) plant name and location; (2) date of the test; (3) sampling location; (4) initials of the sampler(s); (5) run number; (6) material sampled for (in this case, SO_2); (7) barometric pressure; and (8) a number identifying the meter box used and its associated value of Y (the dry gas meter calibration coefficient).

Reference Method 6 specifies that the dry gas meter reading, flow rate, and dry gas meter temperature be recorded at 5-minute intervals. Accordingly, these readings and respective times should be included on the raw data sheets that document sampling.

For Method 6, the volume of effluent sampled at dry standard conditions is calculated according to the following equation:

$$V_{m(std)} = \frac{KYV_m P_{bar}}{T_m}$$

Where:

$V_{m(std)}$ = Dry gas volume expressed at standard conditions, dscm (dscf).

K = 0.3858 ^{o}K/mm Hg (17.64 ^{o}R/in. Hg).

Y = Dry gas meter calibration coefficient.

V_m = Dry gas volume expressed at meter conditions, dcm (dscf).

P_{bar} = Barometric Pressure, mm Hg (in. Hg).

T_m = Dry gas meter temperature, ^{o}K, (^{o}R)

The variables above are discussed in the paragraphs that follow. Where possible, guidelines are provided for checking or verifying that the reported values are within reasonable and expected limits.

The reviewer should note that the reported standard sample volume has the greatest potential for error.

(1) Flow Rate

Reference Method 6 states that the flow rate should be maintained at 1.0 liter per minute $\pm$ 10%, (2.1 standard cubic feet per hour). The reviewer should check that the reported flow rate measurements fall within the acceptable range. Sampling rates that exceed 1.1 L/min are undesirable, because the decreased residence time of the sample within the impingers containing the hydrogen peroxide may result in diminished SO_2 absorption efficiency, which would be ultimately reflected as a negative bias in the measured concentrations of SO_2. (As a note, information is unavailable regarding the magnitude of the flowrate at which this bias becomes significant; thus, the reviewer should be somewhat liberal in interpreting the technical validity of results obtained from sampling at higher than prescribed flow rates.) Low flow rates, on the other hand, will affect the quality of the data only if the amount of SO_2 sampled is insufficient for analysis.

If the reviewer has doubts concerning the validity of the reported flow rates, he may check them by comparison to the average sampling rate, which is easily computed by: (1) subtracting the initial dry gas meter reading from the final reading, (2) correcting the results by multiplying by the meter calibration coefficient, and (3) dividing the corrected volume by the reported sampling time.

(2) Meter Volume (V_m)

A sample volume requirement is neither specified within Reference Method 6 nor within Performance Specifiation 2. The sample volume and sample time requirements specified within the subparts that describe source performance tests are generally adopted for conducting monitor performance evaluations. For example, for fossil-fuel fired steam generators, Subpart D specifies a minimum sampling time of 20 minutes and a minimum sample volume of 0.02 dscm (0.71 dscf).

When the volume is measured in cubic feet, the dry gas meter readings should be reported to a precision characterized by three digits to the right of the decimal point (e.g., 68.035 dscf). This will ensure that the sample volumes are measured to three significant figures.

The reported metered sample volume will, in all likelihood, differ from the sample volume corrected to standard conditions, reflecting volume dependence upon the meter temperature, barometric pressure, and dry gas meter calibration coefficient. Thus, the sample volume at dry standard conditions, rather than the meter volume, should be employed to assess whether the minimum sample volume requirements have been met. However, the reviewer should recognize that sample volumes less than the minimum may be technically valid.

(3) Meter Temperature (T_m)

The measured dry gas meter temperature is used for correcting the metered sample volume to an equivalent sample volume at (dry) standard conditions of standard temperature and pressure.

The dry gas meter temperature should be reported for each set of 5-minute entries. Reporting the temperature to the nearest whole degree is of sufficient precision. Small errors in the temperature measurement have little effect on the calculated SO_2 concentration because the measured temperature is converted to an absolute basis for all calculations. For example, a temperature of 68° F (20° C) becomes 528° R (°R = degree Rankine, absolute temperature scale in English units) or 293° K (°K = degree Kelvin, absolute temperature scale in metric units). The temperature that figures in the volume computation will always be known to three significant figures.

The reviewer should check that the reported average dry gas meter temperature has been correctly determined. The range of meter temperatures usually encountered is between ambient temperature and 15° F above ambient temperature at the meter location.

(4) Dry Gas Meter Calibration Coefficient (Y)

The dry gas meter calibration coefficient (Y) relates the volume measured by the subject dry gas meter to the true volume measured by a gas meter standard. This coefficient is employed in computing the sample volume corrected to standard conditions. The reviewer should check to see whether the value of Y used in the calculations is consistent with the value appearing on the calibration data form.

Reference Method 6, Paragraph 5.1.1, states that dry gas meters are to be calibrated before their initial use and after every use in the field. In order to ensure completeness, the test reports should include data sheets documenting the initial calibration and the post-test calibration check for every dry gas meter used in the monitor performance test.

The data sheet documenting the initial calibration of the dry gas meter should include the data for three (3) calibration runs. The rotameter readings should each be approximately 1 L/min (2.1 dscfh), and the dry gas meter volume readings should each be approximately 0.5 dscf or greater. The regulations require that no individual Y may differ more than 2% from the mean Y. The reviewer should check for conformance with these specifications.

The data sheet documenting the post-test calibration check should include data for at least two runs. The rotameter readings should each be approximately 1 L/min (2.1 dscfh), and the dry gas meter volume readings should each be approximately 0.3 dscf or greater. Again, no individual Y should differ from the mean Y by more than 2%. The mean value of Y obtained from the calibration check should differ by no more than 5% from the mean value of Y obtained from the initial calibration.

If the 5% specification is not met, the dry gas meter is required to be recalibrated as per the initial calibration. This would necessitate a third data form for a dry gas meter. The regulations state that the Y (of the two initial calibrations) that "yields the lower gas volume for each test run is to be used." This requirement is intended to apply to source performance tests rather than to monitor performance tests. An average Y value for monitor performance tests may be more reasonable for these situations.

(5) Barometric Pressure - P_{bar}

The barometric pressure is used in computing the sample volume corrected to standard conditions. The reviewer can reasonably judge the accuracy of the reported barometric pressures in light of the range of pressures that could ordinarily be expected to occur. "Rules of thumb" can be offered: (1) the

Figure 4-6
Example RM6 Sampling Data Form.

GASEOUS POLLUTANT SAMPLING DATA

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Plant Amalgamated Mung, Inc.

Plant Location Leon, Va.

Date 27 Feb 1979

Sampling Location Unit #3, Stack

Initials WMM

Run Number 1

Material Sampled For SO_2

Probe Heater Used? Yes ✓ No ___

Sample Box Number 9

Filter Used? Yes ✓ No ___

Meter Box Number 4

Barometric Pressure 29.38 *

Ambient Temperature 41°F

Clock Time	Dry Gas Meter Reading	Rotameter Setting	Dry Gas Meter Temperature
1023	60.594	2.5 cfm	49
1028	60.786	2.5	49
1033	60.986	2.5	49
1038	61.183	2.5	49
1043	61.383	2.5	49

Have applicable sampling time requirements been met?

Average value correct?

Total Gas Meter Volume 0.789 dcf ✓ = 61.383 − 60.594

Is subtraction correctly performed?

Average Meter Temperature 49

Clean-Up Bottle Number 1

Comments: * See discussion in text.

Has an adequate sample volume been obtained? (For steam generators > 0.71 dscf)

range of pressures ordinarily observed at sea level range between 29 and 31 in. Hg; and (2) for locations above sea level, the pressure decreases approximately 1.0 in. Hg for every 1000 feet. (This rule underestimates the barometric presure above 3000 ft by about 2.5%).

Laboratory Analyses

Accurate laboratory analytical results are essential to the validity of relative accuracy tests because these analyses determine the masses of SO_2 sampled. However, unlike the data generated during sampling, laboratory data are not as abundant and, because of this, they do not permit quite so thorough a review. Nevertheless, data forms documenting laboratory analyses for SO_2 should accompany the relative accuracy sections of monitor test reports. This practice should ensure reporting completeness and promote quality and adherence to Reference Method 6. In addition, thorough documentation will permit the identification and correction of any errors that occur.

SO_2 Analyses

The mass of SO_2 absorbed during sampling is calculated using the following equation:

$$m_{SO_2} = 32.03N(V_t - V_b)V_{soln}/V_a$$

Where: m_{SO_2} = Mass of SO_2 absorbed, mg.

32.03 mg/meq = Equivalent weight of SO_2, mg per milliequivalent (meq) of titrant.

V_t = Average titrant volume, mL (two titrations).

V_b = Volume of titrant required for the blank, mL.

N = Normality of the barium titrant in meq/mL.

V_{soln} = Total volume of solution in which the SO_2 sample is contained (most often, 100 mL), mL.

V_a = Volume of the sample aliquot titrated (most often 20mL), mL.

A review of the analytical phase of Method 6 requires data for all the terms listed above; thus, at a minimum, all these terms should be recorded on the

laboratory data sheets. Sample data sheets accompany this section (see Figure 4-7). The pertinent data will be discussed individually.

(1) Normality (N)

The normality of the barium perchlorate, $Ba(ClO_4)_2$, (or barium chloride, $BaCl_2$) solution used in titrating the samples should be reported to three significant figures; the value should lie within the range of 0.00980 N to 0.0102 N. Reported concentrations that fall outside this range will not affect the results of the analyses as long as sufficient titrant volumes are used.

(2) Volume of Titrant for Blank

The volume of titrant required for the blank V_b should always be reported. The value should be less than 0.5 mL, or reagent contamination is suspect. Without identification of the source and identity of the contamination, it is not possible to assess accurately the impact on the analyses.

(3) Average Titrant Volume

Each SO_2 sample is titrated twice, and the volumes for the two titrations are averaged. Data for all titrations should be recorded on laboratory data sheets. For each set of titrations, the volumes should agree within 1 percent or 0.2 mL, or the titrations are invalid according to Reference Method 6. In summary, three titrant volumes should be reported for each analysis: the volumes from the two titrations and their average.

(4) Volume of Solution V_{soln} and Volume of Aliquot V_a

The volume of solution in which the SO_2 sample is contained and the volume of the aliquot titrated are usually 100 mL and 20 mL, respectively. If these values are consistent throughout the analyses, it is necessary only to state

FIGURE 4-7

EPA REFERENCE METHOD 6 (SO_2 ANALYSIS WORKSHEET

JOB # _____ PLANT NAME/UNIT # _____

ANALYSIS LOCATION _____ ANALYST _____ DATE _____

H_2SO_4 Volume $V_{h(1)}$ (mL)	Ba^{2+} Volume $V_{t(1)}$ (mL)	Ba^{2+} Norm. N_1 (meq/mL)	H_2SO_4 Volume $V_{h(2)}$ (mL)	Ba^{2+} Volume $V_{t(2)}$ (mL)	Ba^{2+} Norm. N_2 (meq/mL)	H_2SO_4 Volume $V_{t(3)}$ (mL)	Ba^{2+} Volume $V_{t(3)}$ (mL)	Ba^{2+} Norm. N_3 (meq/mL)

$N_x = [V_{h(x)}]$ [$N_{H_2SO_4}$] / [$V_{t(x)}$]; $N_{avg} = [N_1+N_2+N_3]/3 =$ 0._____meq/mL

Run ID	Sample Volume V_{soln} (mL)	Aliquot Volume V_a (mL)	Titrant Volume $V_{t(1)}$ (mL)	Titrant Volume $V_{t(2)}$ (mL)	Titrant Volume $V_{t(avg)}$ (mL)	Mass SO_2 M_{SO_2} (mg)	Gas Volume $V_{m(std)}$ (dscf)	SO_2 Conc. C_{SO_2} (ppm_d)
Blank						←$V_{tb(avg)}$		
*								

$M_{SO_2} = [32.03][V_{soln}][N_{avg}][V_{t(avg)} - V_{tb(avg)}] / [V_a]$

$M_{SO_2(*)} = [32.03]$ [ ] [ ] [-]/[ ] = _____mg

$C_{SO_2} = [13.26][M_{SO_2}] / [V_{m(std)}]$

$C_{SO_2(*)} = [13.26][\quad]/[\quad] =$ _____ppm_d

Constants:
32.03 equivalent weight of SO_2
13.26 $ft^3 \cdot ppm_d/m$

this fact on the laboratory data sheets. If sample dilution is due to high SO_2 concentrations, the pertinent dilution factors should be reported.

4.5.4.2 Reference Method 7 - NO_x

Background

EPA Reference Method 7 is applicable for determining dry basis NO_x concentrations in stationary source effluent streams. In applying this method, an effluent sample is drawn via a heated probe into an evacuated flask containing a solution that oxidizes the NO_x to nitrate ion. The nitrate ion is then determined spectrophotometrically using the phenoldisulfonic acid (PDSA) method. According to convention, the NO_x concentration is reported as NO_2.

For testing NO_x monitor relative accuracy, the inlet of the Reference Method 7 probe is placed adjacent to the monitor's probe to ensure that both monitor and reference method are applied to equivalent samples. A relative accuracy test consisting of 9 runs will include 27 Reference Method 7 samples, since 3 samples are defined as one run. NO_x analysis is rarely (if ever) performed in the field during the operational test period because of the extended period required for complete oxidation of the NO_x and because of the need for laboratory hood space.

Review of Method 7, NO_x - Data and Results

If a complete review is to be performed, the documentation of Reference Method 7 sampling must provide sufficient data to recalculate all NO_x concentrations. The novice should note that a substantial amount of data manipulation is required to recalculate the concentrations of NO_x.

In reporting the concentration of NO_x, the greatest potential for error lies in calculating the sample volume, i.e., the volume of effluent sampled on a dry basis and corrected to standard conditions, V_{sc}. The second major source of error occurs in the analysis phase, specifically where the spectrophotometer calibration factor is determined. The review should focus on these two aspects of the report as a minimum.

The following discussions treat individually all the raw data that enter into the determination of NO_x concentrations. Emphasis is placed on the following: (1) the precision requirements of these data; (2) factors affecting these data; and (3) the normal range of values of these data.

Data Reporting

In order to be complete, each raw data sheet should contain the following identifying information (see example sheet): (1) the source name and location; (2) the sampling date; (3) the sampling location, e.g., stack breeching, or duct; (4) the initials of the sampler; (5) run and sample numbers documented on the data sheet; and (6) the material sampled for (in this case, NO_x).

If the reviewer is to recalculate the sample volumes, the data that appear on the raw data sheet should include the following tabulated information and data: (1) the run number; (2) the flask identification; (3) the volume of the flask, V_f; (4) the volume of absorbing solution contained in the flask, V_a; (5) the initial temperature of the flask, t_i; (6) the initial relative pressure of the flask (as measured with a mercury manometer), P_i; (7) the initial barometric pressure, $P_{bar\ i}$; (8) the final temperature of the flask, t_f; (9) the final relative pressure of the flask (measured with a manometer), P_f; and (10) the final barometric pressure, $P_{bar\ f}$.

In order to compute the volume of effluent sampled, it is first necessary to place the initial and final temperatures and pressures on an absolute basis. This is accomplished by adding the standard absolute temperature and the associated barometric pressures, respectively. These and the other data above are then used to compute the standard sample volume using Equation 7-2 in Reference Method 7:

$$V_{sc} = K_1(V_f - V_a)\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right]$$

Where:

P_f = Final absolute pressure of flask, mm Hg (in. Hg).

P_i = Initial absolute pressure of flask, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

T_f = Final absolute temperature of flask, ^{o}K (^{o}R)

$K_1 = P_{std}$ = 0.3858 ^{o}K/mm Hg, metric units (17.64 ^{o}R/in. Hg, English units)

T_i = Initial absolute temperature, ^{o}K (^{o}R).

T_{std} = Standard absolute temperature, 293 ^{o}K (528 ^{o}R).

V_{sc} = Sample volume at standard conditions (dry basis), mL.

V_f = Volume of flask and valve, mL.

V_a = Volume of absorbing solution, mL.

(1) Volume of the Flask and Valve

Reference Method 7 specifies the use of two-liter (2000 mL) flasks for the collection of NO_x samples. The flasks must be equipped with 3-way stopcock valves in order to allow for evacuation and isolation of the sample. The flask

volume (V_f) is the combined volume of the flask and the valve. Reference Method 7 states that the flask volume should be reported to the nearest 10 mL. Thus, the flask volume should be known at a minimum to three significant figures.

The volumes of the flasks will not all be 2000 mL; the reviewer will encounter a range of volumes from 1950 to 2050 mL.

The reviewer should note that the accuracy and precision of the NO_x determination is not affected by the flask volume per se; rather, it is the resultant standard sample volume that potentially affects the quality of the result.

(2) Volume of the Absorbing Solution

A relatively small measured volume of absorbing solution is placed within the sampling flask in order to react with the NO_x and thus trap it for the subsequent laboratory analysis. The volume occupied by the absorbing solution reduces the flask's available volume and, as a result, the calculation of the volume of effluent sampled, corrected to standard conditions (V_{sc}), requires that the volume of absorbing solution (in mL) be subtracted from the flask volume.

Reference Method 7 specifies that the volume of absorbing solution be 25 mL. In most cases, the reviewer will find the absorbing solution volume reported to the nearest mL. Such precision is easily obtained by dispensing the absorbing solution with a graduated cylinder.

The reviewer may safely assume that the volume of absorbing solution may vary between 20 mL and 30 mL without any effect on the quality of the result. Volumes of absorbing solution smaller than 20 mL may be incapable of completely

reacting high concentrations of NO_x. Volumes larger than 30 mL, while not affecting the quality of results, may interfere with the stated methodology of the laboratory phase of the analysis because larger volumetric flasks may be necessary.

(3) Initial Relative Flask-Pressure

The initial flask relative pressure is measured with a mercury manometer. Since the manometer indicates the pressure of the flask relative to barometric pressure and since the flask is under vacuum, the initial flask pressure must be a negative quantity. If the same vacuum pump is used throughout the sampling, the reported initial flask pressures are generally very close in magnitude.

Under conditions of fair weather and elevation not far above sea level, the initial flask relative pressures will normally fall between -26 and -28 in. Hg (-660 mm Hg to -711 mm Hg). This range of values reflects the specified criterion that the initial absolute pressure of the flask must be less than 3 in. Hg (75 mm Hg). Adequate precision is maintained if the pressure is reported to the nearest 0.1 in. Hg (2 mm Hg).

(4) Initial Absolute Pressure of the Flask

This quantity is required by Method 7 to be less than 3 in. Hg (75 mm Hg). Adherence to this criterion ensures that an adequate volume of effluent will be sampled.

(5) Final Flask Pressure

The final flask relative pressure, like the initial flask relative pressure, is measured with a mercury manometer and is thus a relative quantity. Unlike the initial flask pressure, the final flask pressure may be lower

(negative), greater (positive), or equal to barometric pressure. The sign and magnitude of the final flask pressure are dependent on the following parameters: (1) the difference between the stack pressure during sampling and the barometric pressure before clean-up; (2) the pressure of the effluent stream sampled; (3) the moisture content of the effluent stream; (4) the difference between the absolute temperatures during sampling and before clean-up; (5) the evacuated pressure of the flask before sampling; and (6) the presence of leaks in the flask. All relative pressures should be reported to the nearest 0.1 in. Hg (2 mm Hg).

When checking these relative pressure data, the reviewer should recognize first that Method 7 does not address the acceptable range of the data. Second, the reviewer should nonetheless recognize that anomalies in the data may indicate possible problems with sampling and sample integrity. The impact of such problems on the test results generally cannot be quantified; therefore, the reviewer should interpret with caution. The following paragraphs provide example anomalies.

Improper venting of the flasks to the effluent will result in low final relative flask pressures, e.g., -10 in. Hg. While not specifically addressed within Method 7, such situations simply mean that less effluent is sampled, which may potentially affect the precision of the determination.

Final flask relative pressures consistently 0.0 in. Hg in magnitude may be indicative of leaks. This criterion is somewhat difficult to apply because of the potential for coincidence.

Finally, large positive final relative pressures should be viewed with suspicion because, for example, without restraining clips the design of the flask/valve assembly does not permit the build-up of large relative pressures

(greater than 2 in. Hg). Thus, if the Method 7 raw data sheets showed two sets of relative pressures, e.g., flask pressures greater than 2 in. Hg and flask pressures of 0.0 in. Hg, some of the flasks could have vented themselves to the atmosphere. The reviewer would have to assess the significance of venting on a case-by-case basis.

(6) Final Absolute Pressure of the Flask

This quantity is obtained in a fashion analogous to the initial absolute pressure discussed above. As such, the dependencies, precision, and range of values will reflect the final flask relative pressure and the final barometric pressure.

(7) Barometric Pressure (P_{bar})

The reviewer can reasonably judge the accuracy of the reported barometric pressures in light of the range of pressures that could ordinarily be expected to occur. "Rules of thumb" can be offered: (1) Pressures ordinarily observed at sea level range between 29 and 31 in. Hg; and (2) For locations above sea level, the pressure decreases approximately 1.0 in. Hg for every 1000 feet.

(8) Initial Temperature of the Flask (t_i)

The values reported for the initial flask temperatures for the most part reflect the sampling environment, and, as such, must be viewed as being dependent on the weather, the time of day, the time of the year, and the sampling location at the source. Since flasks are ordinarily cleaned up in a laboratory environment, the values reported for the final flask temperatures usually reflect room temperatures.

The reviewer should exercise his own common sense in reviewing the reported temperatures. For example, a reported temperature of 140° F for either the initial or the final flask temperature should be viewed with suspicion because of the obvious limitations of the human body under such conditions.

(9) Volume of Effluent Sampled, Corrected to Standard Conditions (V_{sc})

This value may not be directly accessible to the reviewer, in which case it would be necessary to compute it from the raw data. The value for V_{sc} should lie between about 2000 mL and 1000 mL. Values lower than 1000 mL may be indicative of incomplete venting of the flasks to the effluent or the use of smaller flasks than those specified.

Laboratory Analysis

The laboratory analysis for NO_x provides the mass of NO_x collected. To ensure adherence to the Reference Methods and to promote data quality, it is recommended that data forms documenting the laboratory analyses for NO_x accompany the relative accuracy sections of monitor test reports.

NO_x Analyses

The mass of NO_x absorbed during sampling is calculated using the following equation:

$$m_{NO_2} = 2K_c AF$$

Where: m_{NO_2} = Mass of NO_x (computed and reported as NO_2) absorbed, µg.

K_c = Empirically determined spectrophotometer calibration factor, µg NO_2/unit absorbance.

A = Measured sample absorbance.

2 = Aliquot factor.

F = Dilution factor (used only if necessary).

The review of the majority of the NO_x laboratory data is straightforward and primarily involves checking the accuracy of simple multiplication operations. Errors that may have occurred in the analytical phase, however, cannot be detected by such checks. The parameter, K_c, should be well scrutinized. The parameters important to the analyses for NO_x and which should be included in the test report are discussed individually below.

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(1) Mass of NO_x Sampled (m_{NO_2})

The laboratory data sheets should include the mass of NO_x (in μg) for each acquired sample. The reporting convention for the analysis is that NO_x is reported as NO_2. The reviewer should ensure that a one-to-one correspondence exists between the number of reported masses and the number of reported NO_2 concentrations.

(2) Aliquot Factor (2)

The analytical phase of Reference Method 7 specifies the analysis of a 25-mL aliquot from the total sample volume of 50 mL. Thus, 50 mL/25 mL = 2. If Reference Method 7 is strictly followed, the aliquot factor should be implicit in all the determinations and needs to be shown only in a sample calculation.

The analytical results are not necessarily affected by aliquot factors other than "2." If factors other than "2" are used, they should be reported on the laboratory data sheet, and the deviation from prescribed procedure should be addressed in the text of the report.

(3) Dilution Factor (F)

Occasions arise when sample absorbance is outside the range of the spectrophotometer calibration. The sample must be precisely diluted with water in order to determine the NO_2 concentration in a valid manner. If dilution is required, the appropriate dilution factor should be reported on the laboratory data sheet. If proper laboratory technique is applied, dilution should not affect the quality of the analysis result.

(4) Measured Absorbance of the Sample (A)

For each sample, the absorbance as read from the spectrophotometer should be reported. The values reported will ordinarily range from 0 to approximately 1.5. The absorbances of all samples should be less than the absorbance of the most concentrated calibration standard. The results from samples not meeting this criterion may be biased high.

(5) Spectrophotometer Calibration Factor

The single most important element in the determination of the mass of NO_x sampled is the spectrophotometer calibration factor, K_c. In the analysis phase of Reference Method 7, standards are prepared which cover the linear operating range of the spectrophotometer. A numerical method is then employed to fit the resultant concentrations and associated absorbances to a line, and the slope of the line, K_c, is subsequently used for assigning concentrations to the absorbances indicated by NO_x samples. The value for K_c is computed using the following equation:

$$K_c = \frac{100\ A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2}$$

Where: A_1 = Absorbance of a 100- µg NO_2 standard.

A_2 = Absorbance of a 200- µg NO_2 standard.

A_3 = Absorbance of a 300- µg NO_2 standard.

A_4 = Absorbance of a 400- µg NO_2 standard.

It is highly recommended that all the pertinent absorbances for the determination of the spectrophotometer calibration factor be included within

the data sheets that document the laboratory analysis of NO_x. These absorbances should be correctly labelled so that the value of K_c can be determined by the reviewer. Alternatively, the calibration data can be presented graphically with the calibration points and their associated absorbances well labelled. Example data sheets follow (see Figures 4-8 and 4-9).

The reviewer should check the linearity of the reported calibration. This can be accomplished either through the use of a calculator having a linear least squares program or graphically. (The reviewer should note that the value of K_c afforded by linear least squares will not necessarily equal the value obtained through the use of the equation above. In addition, the reviewer is reminded to include the origin data in the linear least squares computation.)

Ideally, all calibration points should lie on the computed calibration line; this will be obvious if a calibration is checked graphically. Using the calculator, the ideal case would be indicated by a correlation coefficient value of 1.00. (This function is generally included as part of the linear least squares program.)

The current version of Reference Method 7 does not address the precision of the spectrophotometer calibration; thus, neither established guidelines nor specifications are available regarding the limits to which calibration points may deviate from the calibration line before calibration is considered to be of insufficient quality. The reviewer, nevertheless, should recognize the critical importance of the spectrophotometer calibration factor in ultimately providing the NO_x concentration result: the accuracy and precision (i.e., the quality) of the spectrophotometer calibration is a direct factor in determining the reported NO_x concentration.

FIGURE 4-8.

Example Laboratory Data for Reference Method 7

3/6/79

NOx Analyses for Amalgamated Mung. Unit #3

All samples were checked for leakage in transit. No leakage

Sample Number	Absorbance (A)	µg
1	0.634	887
2	0.638	893
3	0.636	891
4	0.608	852
5	0.607	850
6	0.605	847
7	0.570	798
8	0.564	789
9	0.571	800
10	0.637	892
11	0.641	898
12	0.643	900
13	0.615	861
14	0.621	869
15	0.611	855
16	0.606	849
17	0.605	847
18	0.612	857
19	0.620	868
20	0.626	877
21	0.626	877
22	0.534	748
23	0.524	734
24	0.528	739
25	0.572	801

Do the reported µg correspond to the reported absorbances ?

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FIGURE 4-8 (Cont'd.)

8

3/6/79

Sample Number	Absorbance (A)	µg
26	0.574	803
27	0.581	813
28	0.646	905
29	0.648	908
30	0.657	920

Samples analyzed at 413 nm. Dilution was required.*

$A_1 = 0.210$
$A_2 = 0.557$
$A_3 = 0.800$
$A_4 = 1.20$

Is the value reported for K_c correct?

$$K_c = 100 \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2}$$

$K_c = 350$

$\mu g\ NO_2 = 2 K_c A F \quad (F = 2)$*

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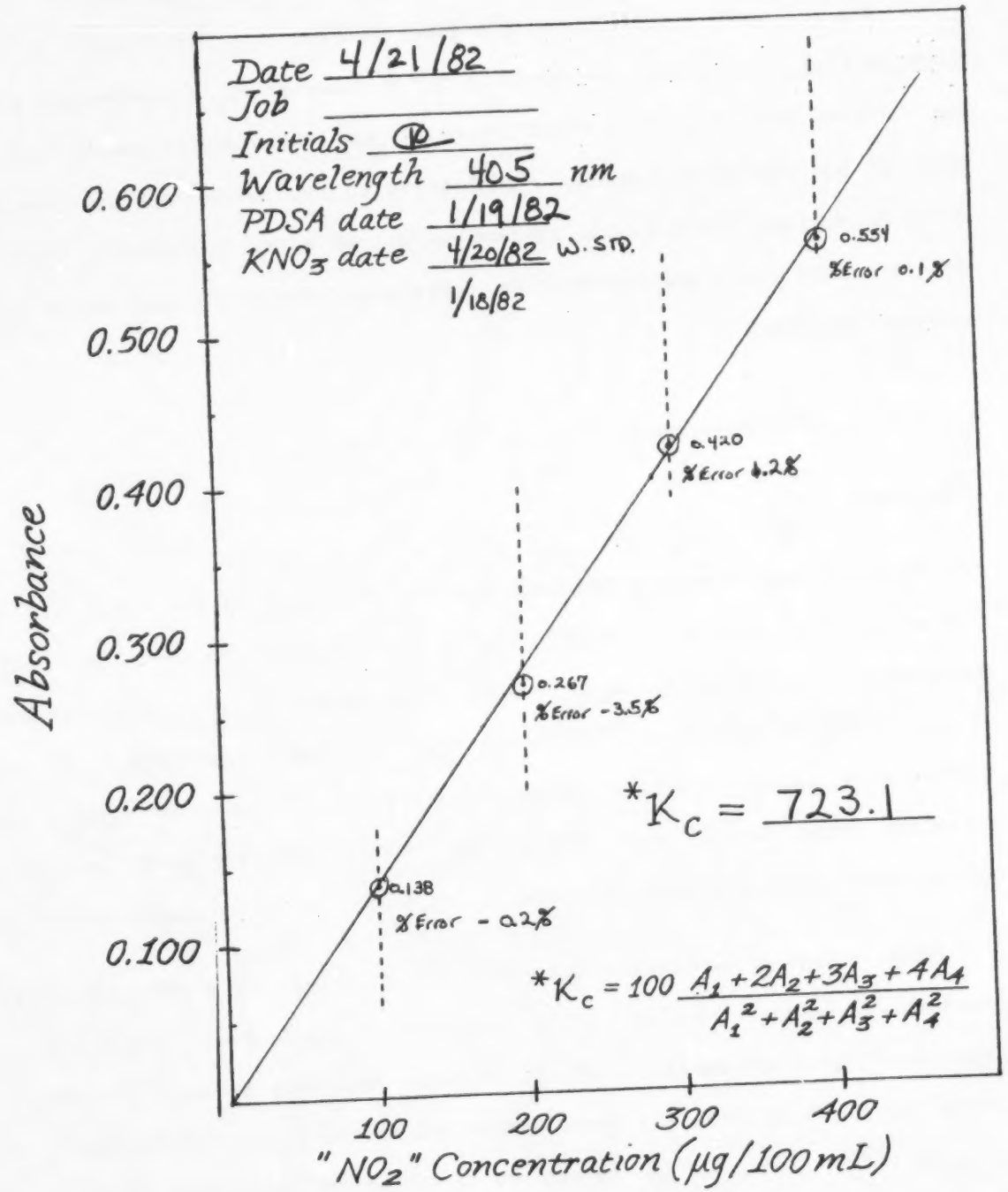
FIGURE 4-9.

Spectrophotometer Calibration Curve for Determination of "NO_2" Using EPA Reference Method 7. Concentration "NO_2" vs. Absorbance.



It is not uncommon for the PDSA method, as ordinarily practiced, to show ± 5% deviations from the calibration line. Indeed, higher deviations (e.g., ± 10%) are not rare, especially at the lower concentration calibration points. Consequently, in assessing the adequacy of the reported NO_x concentration data, the reviewer must weigh the significance of spectrophotometer calibration in light of the precision commonly associated with the method and the reported relative accuracy status of the subject continuous emission monitor. Clearly, the review of the spectrophotometer calibration factor is approached on a case-by-case basis.

4.5.4.3 Moisture Sampling/Moisture Correction Factors

Background

Pollutant concentration measurements are expressed as the ratio of the mass of the pollutant of interest to the total gas sample volume. Wet basis measurements include the quantity of water vapor in the effluent sample as part of the total volume of gas (denominator). Dry basis measurements do not include water vapor as part of the total gas volume. Water vapor dilutes the pollutant concentration; thus, for a given sample, the dry basis pollutant concentration will be greater than the corresponding wet basis concentration.

Many continuous monitors measure gas concentrations on a wet basis. In contrast, Reference Methods 6 and 7 provide pollutant concentration measurements on a dry basis. Thus, it is often necessary to apply a moisture correction factor so that all measurements are on the same moisture basis. A moisture correction factor can be applied to either the monitoring data or the reference method data. However, it is more consistent to apply the correction to the reference method data because these determinations of SO_2, NO_x, and H_2O

all entail classical, i.e., wet-chemical methods, as distinguished from instrumental methods, e.g., continuous monitors. Nevertheless, equally valid results and interpretations will be provided if corrections are applied to the continuous emission monitor data.

The moisture correction factor is determined from the results of effluent moisture measurements. The appropriate monitor sample stream moisture content is not always the same as the effluent moisture content. All in-situ monitors provide wet basis measurements; therefore, the moisture content of the stack gases must be determined for relative accuracy tests. Extractive monitoring systems, on the other hand, may contain conditioning systems that remove moisture from the sample prior to analysis; thus a dry basis measurement may be afforded. Extractive monitors also are available that measure on a wet basis. Finally, there are extractive monitors with sample handling/conditioning systems that remove a portion of the water vapor from the sample stream. Thus, the concentrations indicated by such a monitor are somewhere between dry-basis and wet-basis. For purposes of relative accuracy testing, the moisture basis is generally assumed, for convenience, to be either one moisture basis or the other. The choice is often dictated by the moisture basis of the associated diluent monitor, if such a monitor is used conjunctively. Accordingly, the performance specifications require that such pollutant-diluent combinations must be either total wet basis or total dry basis.

Moisture Sampling

The regulations are not explicit regarding the methodology to be employed in determining moisture correction factors. Performance Specification 2 states, "Determine the correction factor by moisture tests concurrent with the reference method testing periods. Report the moisture test method and the

correction procedure employed." Since the moisture correction factor is an integral part of the relative accuracy calculations, pertinent raw data, sample calculations, and a brief description of methodology should be included in the test report. Also, it is necessary to have a record of each correction factor used, identified according to which reference method test it complements.

Reference Method 4, "Determination of Moisture Content in Stack Gases," describes two sampling methods - a reference method and an approximation method. The reference method employs Smith-Greenburg impingers, whereas the approximation method uses midget impingers. Reference Method 4 is not often used in monitor performance evaluations, because the same information can be obtained through the use of midget impingers, which are also employed in Reference Method 6. Used instead are modified versions of the approximate Method 4, acceptable for monitor performance tests. This modified methodology is described in, "An Alternative Method for Stack Gas Moisture Detemination," by Jon Stanley and Peter R. Westlin. Therein, two alternative sampling procedures are described: (1) a modified approximate Method 4, and (2) a modified Method 6 sampling train used to measure moisture content and SO_2 concentration simultaneously. For both sampling procedures, midget impingers in an ice bath are used as condensers and are followed by a silica gel trap. The sampling train is weighed to the nearest 0.01 gram before and after sampling, thus affording a gravimetric determination of the moisture. The weight gain of the sampling train is used to calculate the moisture content of the sample stream according to the following equations:

$$V_{wc} = 1.336 \times 10^{-3} w$$

Where: V_{wc} = Volume of water vapor condensed, corrected to standard conditions, scm.

w = Total weight gain of the condenser and silica gel trap assembly, g.

Where: V_{mstd} = Dry gas volume measured by meter, corrected to standard conditions, dscm.

Y = Meter calibration coefficient, dimensionless.

P_m = Absolute meter pressure, mm Hg.

T_m = Absolute temperature at meter, ^{o}K

V_m = Dry gas volume measured by meter, dcm.

$$B_{ws} = \frac{V_{wc}}{V_{wc} + V_{m\ std}} \times 100$$

Where: B_{ws} = Water vapor content in stack gas, percent by volume.

The above equations apply to any condenser type moisture method. An example data sheet for condenser methods follows.

Review of Moisture Sampling Data and Results

The reviewer may evaluate the reported moisture sampling results either by checking the raw data and calculations or by checking that the reported results fall within reasonable limits. In particular, the reviewer should check the volume of the effluent sampled, corrected to dry standard conditions, and the subsequent calculation of the sample stream moisture content. The reviewer is directed to the discussion of the review of Method 6 sampling data for procedures explaining the check of effluent sample volume data.

The reviewer should check that all reported moisture contents fall within reasonable limits. For determinations of moisture in effluent streams from fossil-fuel fired steam generators, nomographs are available which allow estimations of the percentage of water vapor in the effluent, based upon: (1) the fuel used, (2) % excess air, (3) free water in the fuel, (4) ambient temperature, and (5) relative humidity (see Fig. 4-10). Even if measured values are not available for all of the parameters listed above, the reviewer should at least be able to bracket the moisture content by using estimated ranges for those various parameters.

It should be emphasized that the moisture content of the stack gases cannot exceed the moisture content at saturation conditions. For example, after the effluent passes through wet scrubbers, stack gases may contain entrained water droplets. In this instance, any condenser type moisture method may yield erroneously high results.

Such situations are addressed within Reference Method 4, which states that if water vapor saturation is suspected within the effluent stream, or if the effluent stream contains entrained water droplets, then, using the effluent stream temperature as a reference, moisture should also be determined simultaneously either by: "(1) using a psychrometric chart and making appropriate corrections if stack pressure is different from that of the chart, or (2) using saturation vapor pressure tables." Method 4 states that the lower of the two moisture determination results shall be considered correct.

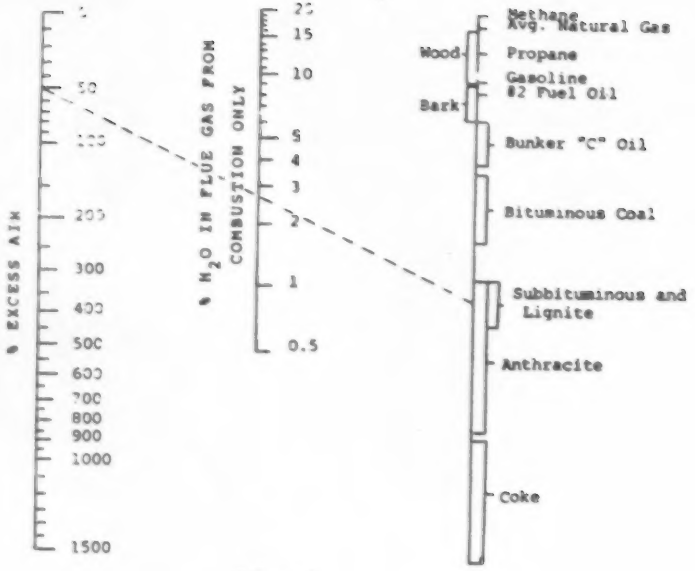


Figure A

FOR DETERMINING MOISTURE IN FLUE GAS FROM COMBUSTION OF FUEL

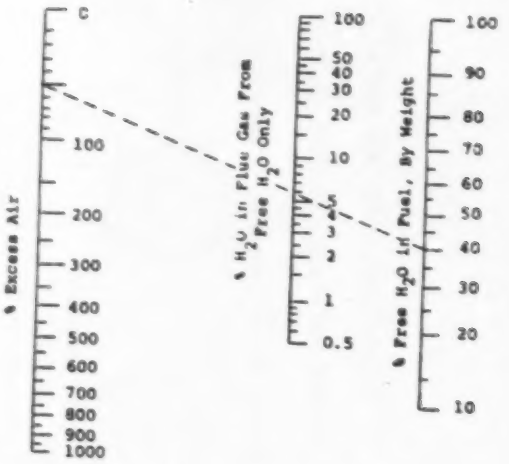


Figure B

FOR DETERMINING MOISTURE IN FLUE GAS FROM FREE WATER IN FUEL

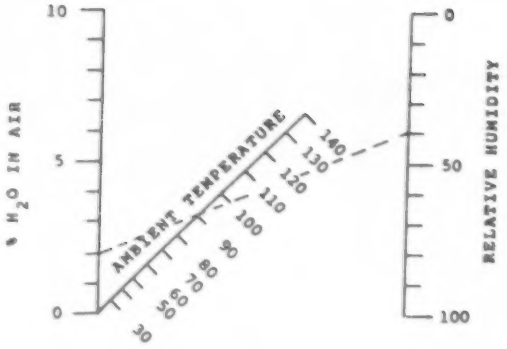


Figure C

MOISTURE FROM THE AMBIENT AIR

ENTROPY ENVIRONMENTALISTS, INC

MUST KNOW:

1) Type of Fuel
2) Free Water in Fuel
3) Humidity of Ambient Air

EXAMPLE: Lignite with 40% free water is burned at 50% Excess Air, which is 90 °F at 40% Relative Humidity. Add 2.5% (from fuel - Figure A), 6% (from free water - Figure B), and 2% (from ambient air - Figure C) to get 10.5% moisture in the stack gases.

NOMOGRAPHS FOR ESTIMATING MOISTURE IN COMBUSTION SOURCES

FIGURE 4-10.

Moisture Correction Factors

Once the moisture content of the stack gas is determined, the moisture correction factor should be calculated and applied to the reference method test results. The following generalized equation is applied to adjust the reference method results from a dry basis to a wet basis:

$$\left[\begin{array}{c}\text{reference}\\ \text{method}\\ \text{concentration}\end{array}\right]_{dry}\left[1-\left(\frac{\%\ H_2O}{100}\right)\right]=\left[\begin{array}{c}\text{reference}\\ \text{method}\\ \text{concentration}\end{array}\right]_{wet}$$

4.5.4.4 Calibration Standards and Calibration

Background

Calibration is the single most important parameter evaluated during performance tests of continuous monitors. Indeed, with the exception of the response time test, all the remaining tests address calibration. Thus, calibration accuracy and precision are quantified by the calibration error test. Calibration stability is quantified on a short-term basis by 2-hour drift tests and on a long-term basis by 24-hour drift tests. Finally, the adequacy of the routine calibration procedure, embodied within the calibration error test, is assessed by the relative accuracy test.

The absolute accuracy of calibration is a critical factor for the calibration error and relative accuracy tests. Put simply, a poorly calibrated instrument is less likely to pass these two tests, because both place strong emphasis on the monitor's response relative to known inputs, e.g., calibration gases (or cells) or effluent samples with concentrations established using reference methods. (The drift tests, on the other hand, entail only measuring monitor response to a constant input; the tests do not explicity address how accurately the monitor should measure this constant input.) Fundamental to a properly calibrated monitor are calibration standards known to a high degree of accuracy and precision.

Performance Specification 2 describes the necessary calibration standards employed during continuous monitor performance tests. For extractive monitors, gaseous pollutant standards are required which have concentrations of approximately 50 and 90 percent of instrument span. (The current Performance Specification 2 does not amplify the interpretation of the word

"approximately". The revisions proposed October 10, 1979, may be used for guidance in this regard. Accordingly, the proposed revisions specify that the gas concentrations be 45 to 55 and 80 to 90 percent of span.) "Calibration gas cells whose concentrations are certified by the manufacturer to be functionally equivalent to these gas concentrations" are also permitted in lieu of gas standards. The performance specification provides assurance that the gas standards are not affected by temporal variations in concentration by stating acceptable components of the gas mixtures, e.g., sulfur dioxide in nitrogen, and by implicitly specifying an expiration date for the analyzed gas mixtures: "triplicate analyses of gas mixtures shall be performed within two weeks prior to use using Reference Method 6 for SO_2 and Method 7 for NO_x."

The concentration assigned to the calibration gas is the average of the three analyses. The criterion for acceptable analytical results is that "each sample test result must be within 20 percent of the averaged result or the tests shall be repeated." This criterion gives testers considerable latitude with regard to the quality of data afforded by determinations of calibration gas concentrations; however, this latitude is attended by the risk that the inaccuracy and imprecision of the calibration gas analyses will compromise the results of the calibration error and relative accuracy tests.

More stringent criteria for acceptable calibration gas analytical results are contained in the revisions to Performance Specification 2 proposed October 10, 1979. Many testers have adopted these criteria in order to ensure that performance tests are not biased by gaseous calibration standards of poor quality.

The performance specifications do not specify the appropriate sampling methodology to be employed in sampling calibration gas cylinders. The

reference methods were developed for sampling effluent streams at close to ambient pressures, while cylinders containing calibration gases are at high pressures. Procedures for sampling from gas cylinders have not yet appeared in the Federal Register; however, P. R. Westlin and J. W. Brown of the U. S. EPA have offered several sampling methods in their paper, "Methods for Collecting and Analyzing Gas Cylinder Samples" (Source Evaluation Society Newsletter, Vol. 3, No. 3, September 1978).

Some modifications of the reference methods are often either possible or necessary, because calibration gases are of defined composition and are also free from impurities. For example, the analysis of sulfur dioxide calibration gases using Reference Method 6 requires no final purge because the absence of sulfur trioxide (SO_3) in the sample obviates the need of the impinger containing isopropanol (IPA). (However, a purge is necessary if an IPA impinger is used because SO_2 is absorbed by IPA.) The analysis of nitric oxide (NO) calibration gases using Reference Method 7 requires modification because of the necessity for having oxygen (O_2) present in the flask to ensure complete reaction of the NO to nitrate. Since the cylinders are oxygen-free, sampling must be interrupted before the flask is totally filled with the calibration gas, and oxygen is then admitted by venting the flask to the atmosphere. This procedure is described in greater detail within Reference Method 7, Paragraph 4.1.2.

Performance Specification 2 allows the calibration error test to be performed either in the laboratory or in the field. While it could be argued that the laboratory option would be an unwise choice, in practice the choice of when and where the calibration error test is performed is ordinarily inconsequential. Accordingly, before initiating the operational test period

testers ordinarily will optimize the monitor's calibration to ensure the successful completion of the performance test. The lost time and effort incurred by an aborted or unsuccessful relative accuracy test are sufficiently great that this test will not be started until the testers are confident that the monitor passed or could pass the calibration error test.

Calibration gases are also required by Performance Specification 3 for evaluations of diluent (oxygen or carbon dioxide) monitors. The reviewer should note that the specifications for concentration ranges and triplicate analyses are similar to those within Performance Specification 2. However, the calibration standards have a diminished role because of the lack of specifications for calibration error and relative accuracy within Performance Specification 3.

Because of the vital role calibration standards play in performance tests of continuous monitors, it is highly recommended that test reports contain data that document and support the concentrations assigned to the standards. For concentrations established using Reference Method 6 or 7, raw data sheets for sampling and analysis should be included. If cells are used during the performance test, the report should include documentation of cell concentration certification.

Review of Calibration Gas Analysis

If possible, the reviewer should check the composition of the calibration gases to ensure that the appropriate diluent gas (nitrogen, air) is used.

The reviewer should check the consistency of the reported calibration gas concentrations by comparing the average values from triplicate analyses with the values reported for use in the calibration error test, drift tests, and

response time test. The triplicate analyses of the calibration gases should be checked in order to confirm the accuracy of the reported average concentrations.

The reviewer should verify that the three individual analyses are each within 20% of the reported average. This criterion is easily attainable. The reviewer should recognize analyses that approach the limit of this criterion may have an effect on the observed monitor performance. However, without additional analytical data, the effect cannot be accurately quantified. For example, if a test report indicated that the monitor did not meet the specification for calibration error and if the calibration gas analyses showed poor precision, the reviewer could reasonably recommend that the calibration error test be repeated with more precisely known calibration gas standards.

Finally, the reviewer should check that the dates of the analyses of the calibration gases are within two weeks of the dates of their use in the tests of the affected monitors. Deviations from this criterion should be judged on a case-by-case basis allowing a liberal interpretation.

The complete review of the analyses of the calibration gases requires review of the reference method sampling and analytical data. The reviewer is directed to the "Review of the Reference Method Data and Results" section of the Relative Accuracy discussion of this manual for guidance in reviewing reference method sampling data, analytical data, and calculations.

Calibration Gas Cell Certification

Continuous monitors do not necessarily provide for the introduction of calibration gases for tests of drift, calibration error, or response time. Used instead are cells containing concentrations of gases functionally equivalent to

the gas concentrations required in tests of extractive monitors. According to Paragraph 6.1.2 of Performance Specification 2 and Paragraph 6.2.3 of Performance Specification 3, the concentrations of gases in the cells are required to be certified by the manufacturer. Analyses of the gases in the cells is not possible. Moreover, there are no simple procedures available for verifying the gas concentrations in the cells. The regulations do not specify what constitutes manufacturer certification.

As a minimum, a statement by the instrument manufacturer or operator regarding the gas concentrations of the cells should be included in the test report. The reviewer should check the consistency of these values in those tests that employ the cells.

4.5.4.5 Monitor Location and Reference Method Sampling Location

Background

Performance Specification 2, Paragraph 4, requires gas monitors to be located so that "measurements can be made which are directly representative, or which can be corrected so as to be representative of the total emissions from the facility." The Performance Specification states that conformance with the requirement of representative measurement location can be accomplished by installing the continuous monitor eight or more equivalent diameters downstream from positions of air in-leakage. Stratification, the condition of non-representativeness, is defined by Performance Specification 2, Paragraph 3.9 as "a condition identified by a difference in excess of 10 percent between the average concentration in the duct or stack and the concentration at any point more than 1.0 meter [3.3 feet] from the duct or stack wall." This stratification definition implies that all locations less than 1.0 meter from a duct or stack wall are suspected of being stratified.

Performance Specification 2 does not contain detailed methodology for determining the degree of stratification; thus, the specification states only that the tester may perform a traverse to characterize any stratification of effluent gases that might exist. The reviewer should recognize that technically valid assessments of stratification must account for the temporal variability of concentrations within the effluent stream. Documents that address valid stratification test procedures are available from the U.S. EPA, SSCD.

If the results from testing indicate the absence of stratification, then the established representativeness of the effluent ensures that the continuous

monitor may be acceptably located anywhere within that location. The converse situation is addressed within Performance Specification 2, which provides, essentially, the choice of either: (1) determining the pollutant concentration in a manner which permits correction to representative conditions, or (2) accounting for the impact of stratification by monitoring the concentration of either oxygen or carbon dioxide. The reviewer should note that no owner or operator of a continuous monitor has opted for the first choice because of the technical difficulty associated with verifying the adequacy of the correction technique. Thus, diluent monitors (continuous monitors for CO_2 or O_2) are employed instead. (Indeed, for sources required to report pollutant emission rates in units of lb NO_x or $SO_2/10^6$ Btu, a diluent monitor, in conjunction with the pollutant monitor, is absolutely essential.) The proper use of a diluent monitor for purposes of accounting for stratification effects implicity requires that the diluent and pollutant monitors measure effluent samples with approximately equivalent composition. This requirement is reflected by the specification that both monitors be of the same "type" (both extractive or both in-situ). Nevertheless, established guidelines regarding the proper placement of pollutant and diluent probes in stratified effluent streams are unavailable. Clearly, the problem is moot if both pollutant and diluent determinations are performed, either on one sample obtained from a common probe or within the same sample path (for in-situ monitors).

Location is an issue that must be considered during the monitor performance test. During the sampling phase of a relative accuracy test, it is imperative that the gas stream sampled according to the reference method is equivalent to the gas stream sampled by the monitor. Performance Specification 2, Paragraph 6.2.2.1 addresses the relative positions of the probe tips for an extractive pollutant monitor and for the reference method during relative

accuracy tests: "For continuous monitoring systems employing extractive sampling, the probe tip for the continuous monitoring system and the probe tip for the reference method sampling train should be placed at adjacent locations in the duct." However, the distance implied by the word "adjacent" is not quantified. Also, the above criterion is applicable only to extractive and in-situ monitors that analyze at a point within the effluent. The performance specification does not provide guidance regarding the relative placement of reference method sampling probes when tests of multipoint extractive monitors or across-stack in-situ monitors are performed. A technically valid approach would be to traverse the monitor measurement path with the reference method probe.

Reporting and Review

The issue of monitor location should have been settled long before the monitor performance test is conducted. Nevertheless, the reviewer should, to be thorough, check the drawings included in the test report to confirm that the monitor location is acceptable. The reviewer should approach the relative locations of monitor and reference method probe tips in a similar fashion.

To permit such review, the monitor performance test report should contain a drawing that shows the position of the monitor in the effluent stream. This drawing should display approximate distances from the monitor to: (1) the walls of the stack or duct; (2) control equipment, such as precipitators or scrubbers; (3) points or sources of air in-leakage; and (4) points at which gas streams with dissimilar gas concentrations are combined. (Performance Specification 2 requires that the monitors be located eight or more stack diameters downstream of any positions of air in-leakage. Equivalent diameters for non-circular ducts are defined in 40 CFR 60, Appendix A, Reference Method

1). This same downstream distance criterion should also be applied to points where dissimilar gas streams are combined.

The reviewer should examine the monitor location drawings to verify that the monitor is installed sufficiently far downstream of potential sources of stratification. The reviewer should also check to be sure that single point or short path length monitors are installed to sample more than one meter (3.3 feet) from the stack wall.

If tests were conducted to detect or to quantify stratification of the effluent, a brief statement of the results of these tests should be included in the monitor performance test report. The reviewer should examine these results in order to attempt to verify that the monitor sampling location provides measurements representative of the entire effluent stream.

The relative positions of the monitor sampling region and the probe tip of the reference method sampling train should be illustrated. These positions could be indicated on the drawing showing the position of the monitor in the effluent stream, or the sampling positions could be the subject of a separate drawing. Distances should be indicated in the drawing so that these positions can be fixed.

Performance Specification 2 states that the probe tip of an extractive monitor and the probe tip of the reference method sampling train should be placed at adjacent locations in the duct during field tests for relative accuracy. The reviewer must decide whether the locations meet the definition of "adjacent," bearing in mind that the intent of the word "adjacent" is to ensure that the monitor and probe are sampling identical effluent streams. Separation distances up to approximately 20 cm (8 inches) between the reference method sampling probe and continuous monitor sampling region are usually

considered to be "adjacent." It should be emphasized that if the monitor and sampling probe are not sampling at exactly the same location, and if the issue of stratification has not been resolved, then the failure of a relative accuracy test may be due to the effect of stratification as opposed to monitor inaccuracy.

5.0 REVIEW OF TEST PROCEDURES, DATA, AND RESULTS OF MONITOR PERFORMANCE TESTS FOR CO_2 AND O_2 MONITORS

5.1 BACKGROUND

At fossil-fuel fired steam generators subject to NSPS regulations (40 CFR 60, Subparts D and Da) diluent monitors are required in addition to pollutant monitors. Diluent monitors enable emission rate measurements in units of the standard, lb pollutant/10^6 Btu heat input (ng pollutant/Joule heat input). The diluent gas measured by the diluent monitor may be either CO_2 or O_2. The pollutant gas monitor and diluent monitor must measure on the same basis (i.e., they both measure on either a dry or a wet basis). This requirement is stated in 40 CFR 60, Subpart D, Paragraph 60.45(e)(1).

Because either CO_2 or O_2 can be measured, and because emission rate measurements can be performed either on a wet or a dry basis, a number of equations for calculating the emission rates exist. Some that are commonly used appear below:

Dry Basis (No moisture correction)

$$E = D_c F \left[\frac{20.9}{20.9 - \%\ O_{2d}} \right]$$

$$E = C_d F_c \left[\frac{100}{\%\ CO_{2d}} \right]$$

Wet Basis (Moisture correction)

$$E = C_w F_w \left[\frac{20.9}{20.9\ (1 - B_{wa}) - \%\ O_{2w}} \right]$$

$$E = C_w F_c \left[100/\%\ CO_{2w} \right]$$

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Where: E = Pollutant emissions, lbs pollutant/10^6 Btu (ng/Joule).

C_d = Pollutant concentration, dry basis, lb/dscf (ng/dscm).

C_w = Pollutant concentration, wet basis, lb/scf (ng/scm).

F, F_c, & F_w = Constants determined by the identity of the fuel combusted combusted and the diluent measured. F accompanies measurement of O_2 and F_c accompanies the measurement of CO_2. Both of these constants are on a dry basis. F_w accompanies measurements of O_2 on a wet basis.

$\%O_{2_d}$ and $\%O_{2_w}$ = % concentration of O_2, dry and wet basis, respectively.

$\%CO_{2_d}$ and $\%CO_{2_w}$ = % concentration of CO_2, dry basis and wet basis, respectively.

B_{wa} = Mole fraction of moisture in the combustion air.

B_{ws} = Mole fraction of moisture in the effluent.

Because the factors F, F_c and F_w are constants, measurements of the pollutant and diluent concentrations (and as necessary, the moisture content) provide a basis for calculating the emissions in units of the standard. (For a more detailed presentation of emission rate calculations, the reviewer is referred to 40 CFR 60, Appendix A, Reference Method 19.)

Performance specifications and test procedures for diluent monitors are contained in 40 CFR 60, Appendix B, Performance Specification 3. These specifications and test procedures are very similar to those for pollutant gas

monitors. The performance specifications for diluent monitors are tabulated below.

Parameter	Specification
Zero drift (2h)*	$\leq$ 0.4% O_2 or CO_2
Zero drift (24h)*	$\leq$ 0.5% O_2 or CO_2
Calibration drift (2h)*	$\leq$ 0.4% O_2 or CO_2
Calibration drift (24h)*	$\leq$ 0.5% O_2 or CO_2
Operational Period	$\geq$ 168 h
Response Time	$\leq$ 10 min

(* Expressed as sum of absolute mean value plus 95% confidence interval of a series of tests.)

Major differences between performance specifications for pollutant gas monitors and for diluent monitors include the absence of specifications for relative accuracy and calibration error. Another difference between the specifications is the use of units of concentration (% O_2 and % CO_2) for the drift specifications. This difference reflects the fact that the sum of the absolute mean value and the 95% confidence interval is not subsequently divided by the instrument span. Thus, the diluent performance specifications are expressed on an absolute basis as a % O_2 or a % CO_2, rather than on a relative basis as a percentage of the measured quantity. (The use of % in both cases often creates confusion.) Finally, the response time specification is 10 minutes for diluent monitors as opposed to the 15 minute specification for pollutant gas monitors.

The zero and calibration drift tests and the response time tests for diluent monitors are conducted in an identical manner to those of pollutant gas monitors. The associated calculations are also performed in the same manner, with the exception that final division by the span of the instrument is not performed.

5.2 REVIEWING DILUENT MONITOR PERFORMANCE TEST REPORTS

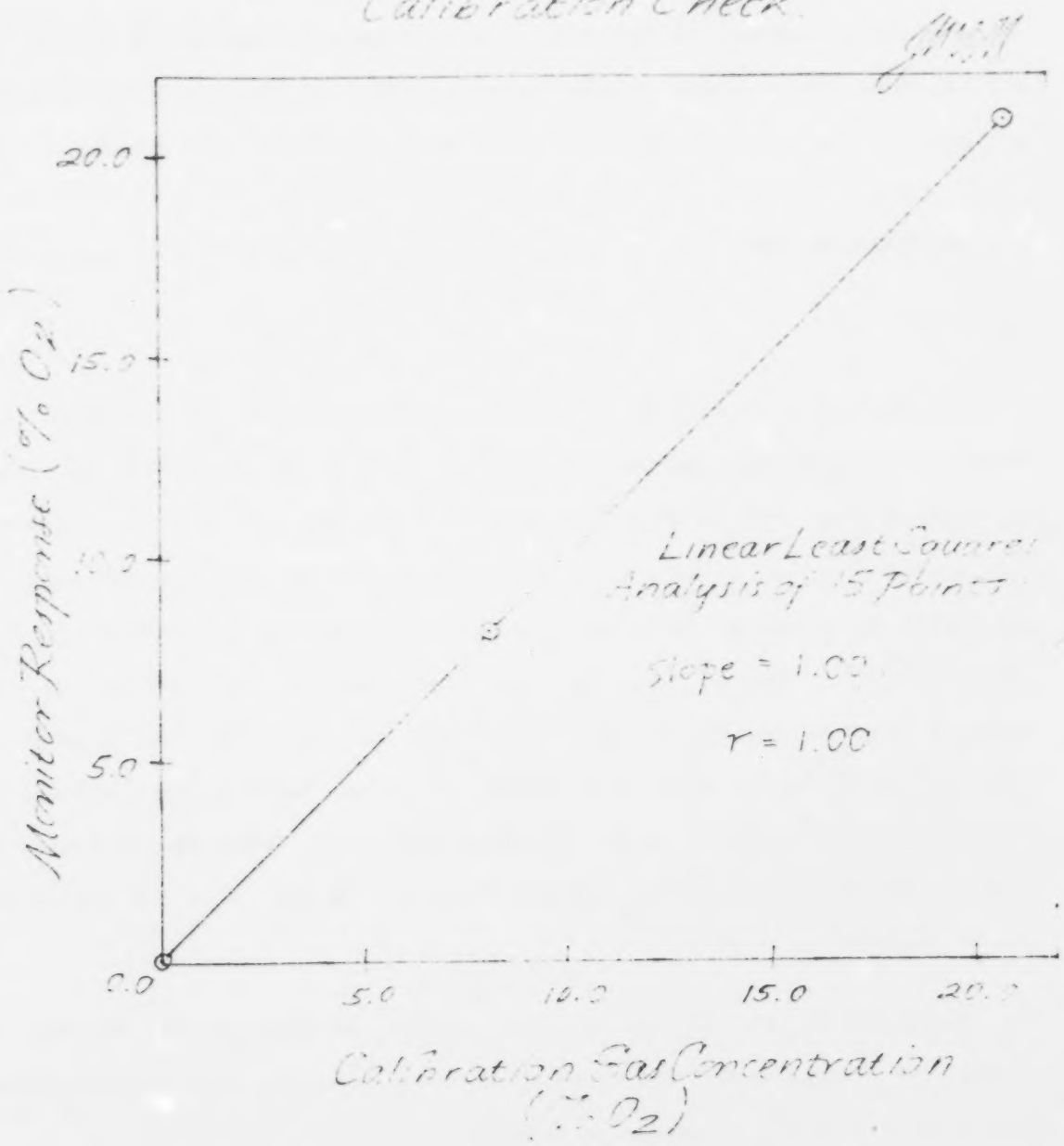
The information and data recommended for inclusion within performance specification test reports for diluent monitors are identical to those recommended for pollutant gas monitors with respect to determinations of calibration values, drifts, and response times. Again, it is important to note that relative accuracy tests and calibration error tests are not included in diluent monitor performance evaluations. The absence of both the relative accuracy test and the calibration error test and their attendant data leaves little (relative to reports for tests of pollutant gas monitors) to report, and therefore, to review.

Although no test per se is required for determining calibration error, a calibration check of the diluent monitor is required by Paragraph 6.1 of Performance Specification 3. Accordingly, the calibration check entails establishing a calibration curve using zero, midrange and span concentration gas mixtures. This resultant curve is then compared with the expected calibration curve as described by the analyzer manufacturer, and its "consistency" is verified. Additional calibration gas measurements are made or "additional steps are undertaken" if the expected response is not obtained. "Consistency" is not defined within the paragraph.

As a minimum, copies of the calibration curves should be provided within the report in order to document that the check was performed. An example is given with Figure 5-1. Raw data forms which document the response time test, the drift tests, and the calibration checks should be included in the monitor performance test report. The reviewer should check the data from the calibration check and should evaluate these data in light of the verified results from the drift tests.

Figure 5-1

Example Data from Calibration Check of Diluent Monitor



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Since the tests for drift and response time are nearly identical to those for gas monitors, the reviewer is directed to those sections in this manual where review procedures for pollutant gas monitors are discussed in detail. As a final note, the reviewer should recognize that mid-range calibration gases are used for the 2-hour calibration drift test rather than span gases.

5.3 CALIBRATION GASES

Background

In a manner analogous to performance evaluations of pollutant gas monitors, diluent monitors require gases of known concentations for the tests of response time, zero drift and calibration drift, and for calibration checks. Calibration gases are injected into extractive monitors, while in-situ monitors may employ certified gas cells functionally equivalent to the required diluent concentrations. Because the reporting requirements for in-situ diluent monitors are identical to those for pollutant gas monitors, the reviewer is directed to the pertinent discussions in this manual (see Calibration Standards, Section 4.5.4.4). The following discussion addresses the reporting requirements applicable to the concentrations of the gas cells and the review of the reported information.

Depending on whether the diluent monitor measures carbon dioxide or oxygen, the composition of the calibration gas mixture is required to be either carbon dioxide in air or oxygen in nitrogen.

The required concentrations of the diluent calibration gases are determined by the "normal carbon dioxide or normal oxygen concentration in the stack gas of the affected facility." Thus, according to Performance

Specification 3, Paragraph 3.2, the span of the instrument "shall be set no less than 1.5 to 2.5 the normal carbon dioxide or normal oxygen concentration." The concentration of the span diluent calibration gas is required to be 90% of the instrument span. The concentration of the mid-range diluent calibration gas is required to be "representative of the normal conditions [oxygen and carbon dioxide concentrations] in the stack gas of the affected facility at typical operating rates." This requirement appears in Paragraph 3.3 of Performance Specification 3. Finally, Performance Specification 3, Paragraph 2.2 permits the use of ambient air as a diluent calibration gas. This provision applies strictly to oxygen analyzers with spans set higher than 21% O_2.

The reviewer may also check the reported concentrations of the span and mid-range gases with regard to the criterion that these should reflect the diluent concentrations present in the effluent during normal operation of the affected facility. The concentrations can be checked for reasonableness by consulting nomographs especially made for the purpose of estimating the concentrations of oxygen and carbon dioxide in the effluents of fossil-fuel fired steam generators. These nomographs can provide limits, which are dependent on the fuel combusted, for the diluent concentrations. It is, however, difficult for the reviewer to fix accurately the "normal" diluent concentration. Most of the problem stems from the large ranges of diluent concentrations encountered at fossil-fuel fired steam generators: 6-15% CO_2 and 3-20% O_2.

The calibration gases for extractive diluent monitors are required to be analyzed within two weeks of their use in monitor performance tests. The gases are analyzed in triplicate, using the methodology of Reference Method 3 —

Orsat analyses of bag samples obtained from gas cylinders. Unlike the paragraph treating the analyses of calibration gases for pollutant gas monitors, the analogous paragraph for diluent monitors does not give a criterion for the acceptability of the results of the triplicate analyses.

Reference Method 3, however, provides requirements for maintaining precision. Paragraphs 4.2.6.1 and 4.2.6.2 of Reference Method 3 address the acceptable criteria for the respective Orsat analyses of CO_2 and O_2. For CO_2, Orsat analysis is repeated "until the results of any three analyses differ by no more than (a) 0.3 percent by volume when CO_2 is greater than 4.0 percent, or (b) 0.2 prcent by volume when CO_2 is less than or equal to 4.0 percent." For determinations of O_2, the criteria are similar: the analysis is repeated "until the results of any three analyses differ by no more than (a) 0.3 percent by volume when O_2 is less than 15.0 percent, or (b) 0.2 percent by volume when O_2 is greater than 15.0 percent." For the analyses of CO_2 and O_2, the average of the three acceptable results is reported as the appropriate concentration. Thus, the criteria for the acceptability of the analyses of diluent calibration gases are very similar to those that apply to pollutant calibration gases.

The test report should contain documentation of the triplicate analysis of all diluent calibration gases used during the monitor performance test.

The review of the analyses of O_2 and CO_2 calibration gases is simple, since the methodology (Orsat analysis of bag samples obtained from cylinders) generates a small amount of data and does not require further manipulation. For an example, see Figure 5-2. The reviewer should first confirm the completeness of the data by checking that each diluent calibration gas used in the performance test is accompanied by a triplicate analysis. Each of the individual analyses for the gases should meet the acceptability criteria

FIGURE 5-2
ORSAT FIELD DATA

Plant Name Analysis of Calibration Gas
Sampling Location Lab
2/14/79

Run and/or Sample No. 1 Leak Test? ✓ Date 2/14/79 Operator [illegible]

Time of Sample Collection	Time of Analysis	CO_2 Reading A	O_2 Reading B	CO Reading C	$\%O_2$ B-A	%CO C-B	$\%N_2$ 100-C
0800	0810	—	8.1	—	8.1		—
"	0830	—	8.0	—	8.0		—
"	0855	—	8.1	—	8.1		—
	Avg.	—		Avg.	8.1		

← Is average correct?

Run and/or Sample No. _____ Leak Test? _____ Date _____ Operator _____

Time of Sample Collection	Time of Analysis	CO_2 Reading A	O_2 Reading B	CO Reading C	$\%O_2$ B-A	%CO C-B	$\%N_2$ 100-C
	Avg.			Avg.			

Run and/or Sample No. _____ Leak Test? _____ Date _____ Operator _____

Time of Sample Collection	Time of Analysis	CO_2 Reading A	O_2 Reading B	CO Reading C	$\%O_2$ B-A	%CO C-B	$\%N_2$ 100-C
							—
							—
							—
	Avg.			Avg.			

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discussed above.

The reviewer should then verify that all the subtraction operations required by the Orsat analysis are correct, and that the reported average diluent gas concentration is also correct. All reported average diluent gas concentrations should be compared as appropriate to the concentrations reported in the drift test, response time test, and calibration check. The reported values should be consistent. Finally, the reviewer can check the time between the analysis of the gases and their use in the performance test. This time interval should be less than 2 weeks; however, the reviewer should bear in mind that diluent calibration gas concentrations are generally very stable.